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SYNTHESIS, CHARACTERIZATION, AND REACTIONS OF A MACROCYCLIC TRANS-DIMETHYL COBALT COMPLEX

MARK WILLIAM WITMAN

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SYNTHESIS, CHARACTERIZATION, AND REACTIONS OF A
MACROCYCLIC TRANS-DIMETHYL COBALT COMPLEX

BY

MARK W. WITMAN

B. S., St. Lawrence University, 1971

A THESIS

Submitted to the University of New Hampshire

In Partial Fulfillment of

The Requirements of the Degree of

Doctor of Philosophy

Department of Chemistry

September, 1976

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This thesis is dedicated to my wife, Christine, and
to my parents.

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ABSTRACT

SYNTHESIS, CHARACTERIZATION, AND REACTIONS OF A MACROCYCLIC TRANS- DIMETHYL COBALT COMPLEX

BY

MARK W. WITMAN

The synthesis of the trans- dimethyl cobalt complex $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ is reported. (BDM1,3pn) is a mononegative tetradendate dioxime-diimine ligand formed by the condensation of two moles of 2,3-butanedionemonoxime and 1,3-propanediamine). The complex was characterized by elemental analysis, electronic, ^1H -NMR and IR spectroscopy. The deuterium labeled complex $(\text{CD}_3)_2\text{Co}(\text{BDM1,3pn})$ was also synthesized and characterized.

The reactivity of the dimethyl complex was compared to that of the corresponding monomethyl complex $[\text{CH}_3\text{Co}(\text{BDM1,3pn})\text{H}_2\text{O}]\text{ClO}_4$. Cobalt-carbon bond cleavage may be induced photochemically both in solution and in the solid state. Under anaerobic conditions solution photolysis yields methane and $\text{Co(I)}(\text{BDM1,3pn})$. Evidence is presented for a homolytic mechanism based on kinetic and mass spectral results.

In contrast to the monomethyl complex, $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ is readily dealkylated by a variety of electrophiles including Ag^+ , H_3O^+ , Zn^{2+} , Cd^{2+} , Pb^{2+} , HgCl_2 , Cu^{2+} , and Cr^{3+} . The products of the reactions with excess metal ion are $\text{CH}_3\text{Co}(\text{BDML},3\text{pn})^+$ and unstable CH_3M^+ or CH_3M . Kinetic studies were conducted on the reactions of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with excess H_3O^+ , Zn^{2+} , and Cd^{2+} . The reaction with H_3O^+ followed simple second-order kinetics, whereas the reactions with Zn^{2+} and Cd^{2+} revealed the presence of binuclear intermediates of the type $[\text{M} \cdot (\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})]^{2+}$.

The reactions of excess $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with Zn^{2+} , Cd^{2+} and Pb^{2+} result in the formation of unstable $(\text{CH}_3)_2\text{M}$ species as evidenced by spectral titrations, methane evolution data, and the identification of the ultimate products.

INTRODUCTION

Compounds with metal-carbon bonds have been known for sometime and it is now clearly recognized that the formation of bonds to carbon is a general and characteristic property of all of the d-group transition metals (1). The development of organocobalt chemistry in particular can be traced to the isolation and characterization of the naturally occurring cobalt corrinoid 5'-deoxy-adenosylcobalamin (Fig. 1). The unique feature of this compound is the cobalt-carbon bond, and its presence was unambiguously confirmed by an X-ray analysis carried out by Professor Hodgkin and her associates at Oxford in 1961 (2). This discovery led to an explosion of activity amongst organometallic chemists in an effort to synthesize new organocobalt complexes for study (3-6).

Further interest in organocobalt complexes resulted from the revelation that other organocobalamins were fundamental to a number of biological alkyl-transfer reactions. For instance, it is now well established that enzyme-bound methylcobalamin, (a methyl group replaces the 5-deoxyadenosine moiety in Fig. 1) is formed as an intermediate in the in vivo synthesis of methionine from N⁵-methyltetrahydrofolate and homocysteine (Fig. 2) (7,8). Other biological methyl-transfer reactions involving methylcobalamin include the biosynthesis of methane and

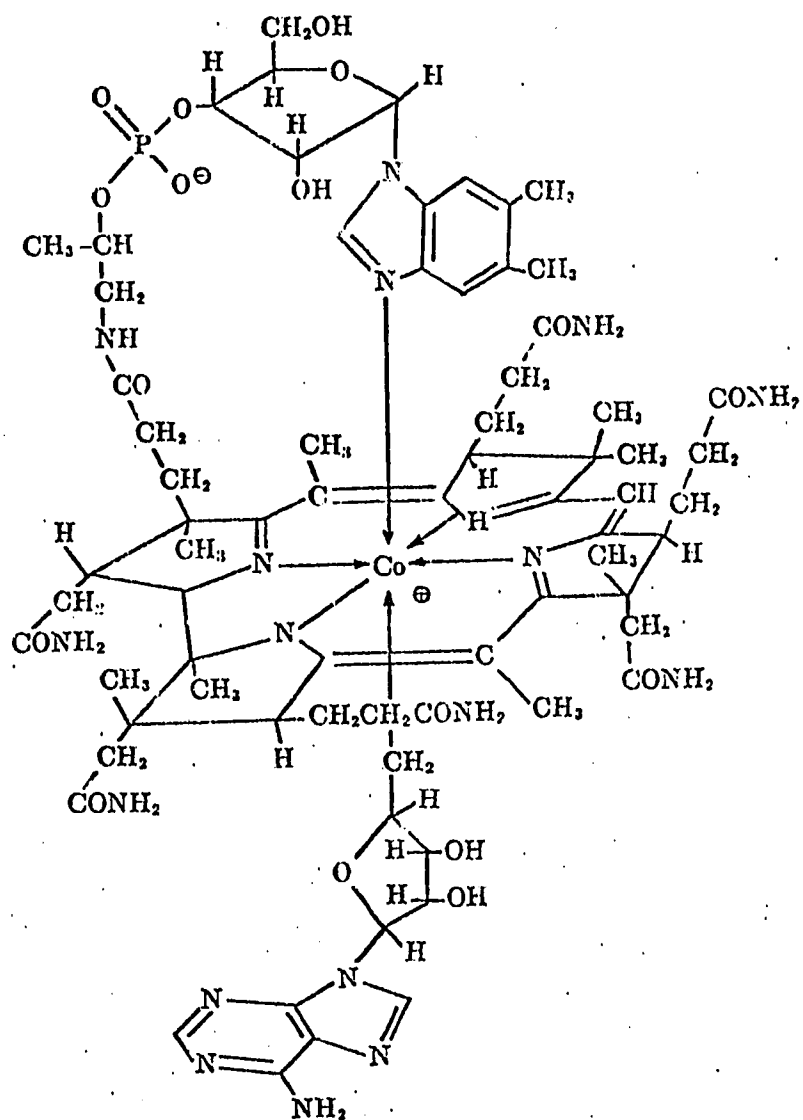


Figure 1. Structure of 5'-deoxy-adenosylcobalamin

acetate (8).

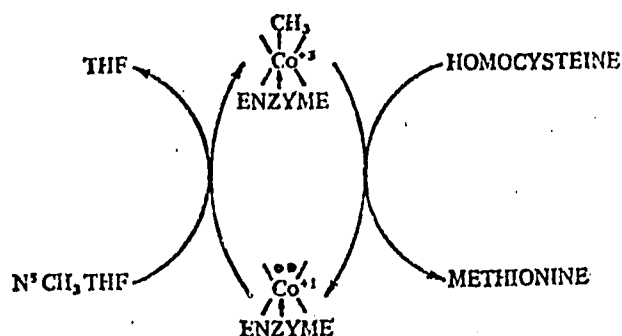


Fig. 2 Proposed Mechanism for Methionine Synthesis

Of particular interest to this work is the more sinister biological role methylcobalamin plays as an intermediate in the microbial methylation of metal ions and metalloids in the environment, which results in the formation of the more toxic methylated derivatives. These reactions are best exemplified by the enzymatic methylation of Hg^{2+} (9) and arsenate (10,11) by methylcobalamin to give methylmercury and dimethylarsine as products. Similar reactions have been demonstrated for selenium and tellurium (11). More recently Wong et al. (12) provided the first evidence for the enzymatic methylation of certain inorganic and organolead compounds in an aqueous system. On the basis of many carefully controlled experiments they confirmed that microorganisms in lake water and sediment were able to convert PbCl_2 , $\text{Pb}(\text{NO}_3)_2$ and $(\text{CH}_3)_3\text{Pb}^+$ into tetramethyllead. Presumably these

reactions also require enzyme-bound methylcobalamin, although the appropriate experiments have not been completed. These enzymatic methyl-transfer reactions have been the subject of several recent reviews, and will not be discussed further (13,14).

The realization that the porphyrin like corrin ring was an important factor in the stabilization of the cobalt-carbon bond, led to speculation that other organocobalt complexes could be prepared by employing analogous tetradentate ligands. The success of this thinking is best illustrated by two recent reviews (15,16) which summarize the nearly 1,000 organocobalt complexes that have been prepared, and by the fact that many of the properties of the naturally occurring cobalamins are indeed manifested by a variety of synthetic cobalt chelates. A particularly significant parallel is the ability of the synthetic ligands to stabilize a redox series of Co(III), Co(II), and Co(I) oxidation states (17-19). This factor appears to be of fundamental importance in the making and breaking of cobalt-carbon bonds.

The synthetic organocobalt complexes which will be discussed here can be categorized according to the number of σ -bonded organo-ligands. Both mono- and bis-organocobalt complexes are known. The former category has been well studied, and is the main focus of the previously mentioned reviews. Examples of bis-organocobalt complexes

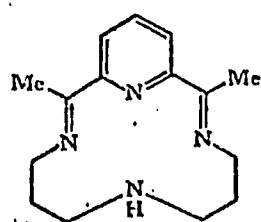
are fewer in number, and very little is known concerning their reactivity. Since the objective of this work was to prepare a dimethyl cobalt complex of the tetradentate ligand BDML,3pn* (see Fig. 3) and to study its reactivity, this discussion will emphasize the syntheses and chemical reactions of bis-organocobalt complexes.

In view of the similarity of the two categories of complexes however, it is desirable first to survey some of the reactions by which Co-C bond is made and broken with regard to the mono-organometallic compounds. This will be done in a general way, and an emphasis will be placed on those reactions which have some bearing on the future discussion of the bis-organocobalt complexes or the experimental portion of this manuscript. The reader should consult the previously mentioned reviews (15,16) or the treatise by Pratt (8) for specific examples of reactions or additional information concerning the properties of the mono-organocobalt complexes.

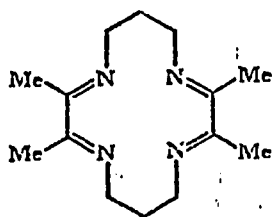
Mono-organocobalt Complexes

The first examples of such cobalamin analogues were reported in 1964 when Schrauzer and Kohnle (20) synthesized stable organobis(dimethylglyoximato)cobalt(III)

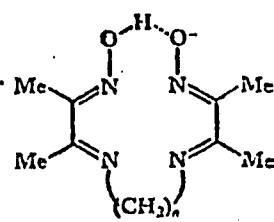
*BDML,3pn; 2,3,9,10-tetramethyl-1,4,8,11-tetra-aza-undeca-1,3,8,10-tetraen-11-ol-1-olato.



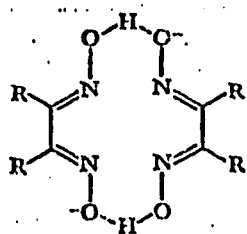
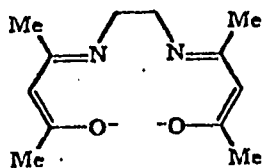
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tim

 $n = 3$

BDM1,3pn

 $R = H$; DMG

acacen

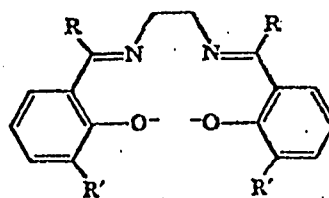
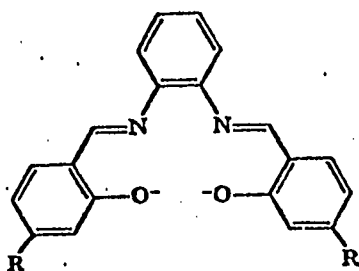
 $R, R' = H$; salen $R = CH_3$; 7,7'-(CH_3)₂salen $R = H$; saloph

Fig. 3. Structures of Chelating Ligands

complexes from bis(dimethylglyoximato)cobalt(I) and organic halides (Eqn. 1). These complexes (cobaloximes)



have been the subject of intensive subsequent studies (21-23). In addition, numerous other cobalamin analogues have been recognized, the study of which has been advanced particularly by Costa and his collaborators (19,24). Complexes of this type $\text{RCo}(\text{chel})\text{B}^*$ ($\text{R} = \text{alkyl, aryl}$; $\text{B} = \text{H}_2\text{O}$, amines, phosphines or absent) are most often six-coordinate with a pseudooctahedral configuration, or in some cases five-coordinate with a square pyramidal

*chel- (dmg)₂, bis(dimethylglyoximato); sal₂en, (bis(salicylaldehyde)1,2-ethane); BDML₃pn 2,3,9,10-tetramethyl-1,4,8,11-tetra-aza-undeca-1,3,8,10-tetraen-11-ol-1-olato; saloph, (N,N'-o-phenylenebis(salicylideneiminato)); tim, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; cr, 2,12-dimethyl-3,7,11,17-tetraazabicyclo(11.3.11)-heptadeca-1, (17), 2,11,13,15-pentaene; acacen, N,N'-ethylene-bis(acetylacetoneiminato) dianion; 7,7'-(CH₃)₂salen, N,N'-ethylenebis(7,7'-dimethylsalicylideneiminato); and others.

configuration (i.e. $\text{chel} = \text{sal}_2\text{en}, \text{acacen}$). In both geometries (Fig. 4) the four equatorial positions are

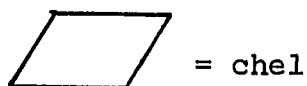
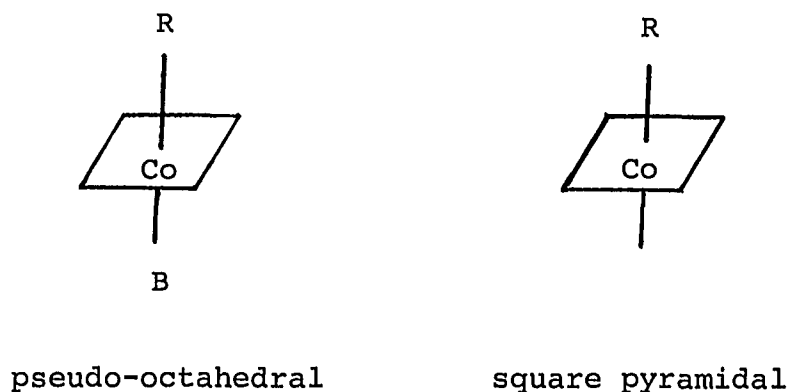


Fig. 4 General Structures of Mono-organocobalt Complexes

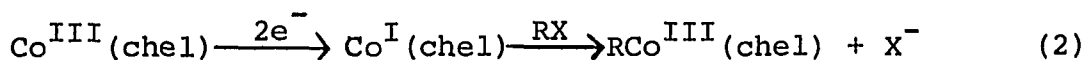
occupied by the donor atoms of the chelating ligands. As can be seen in Figure 3 the donor atoms of these ligands are predominantly N_4 or N_2O_2 , and all are members of a conjugated system with the exception of CR in which one nitrogen is tetrahedral.

Formation of Cobalt-Carbon Bonds

According to the usual conventions the oxidation state of cobalt in organocobalt complexes is +3 while the organic ligand is regarded as anionic (i.e., R^-). By

means of these designations three limiting processes can be considered to lead to the formation of cobalt-carbon bonds: (1) reaction of Co(I) complexes with electrophiles, (2) reaction of Co(III) complexes with nucleophiles, and (3) reaction of Co(II) complexes with radicals.

The reactions of Co(I) complexes with electrophilic agents is the most widely used route to organocobalt chelates. The Co(I) complexes are very powerful nucleophiles (typical Pearson nucleophilic reactivity constants are in the region of $\mu = 14$) (25), and they undergo rapid oxidative addition reactions with a variety of electrophiles. This method of synthesis involves the reduction of the appropriate Co(III) or Co(II) starting material in situ using reducing agents such as sodium borohydride or sodium amalgam, followed by the addition of any one of a number of alkylating agents such as alkyl halides or dialkyl sulfates (Eqn. 2). An alternative



R = alkyl, allyl, benzyl, fluoroalkyl, etc.

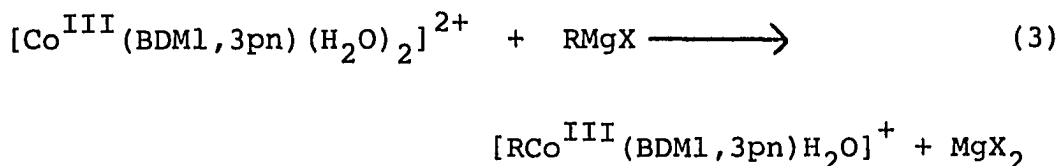
X = Cl^- , Br^- , I^- , $1/2 \text{SO}_4^{2-}$, etc.

method of generating the $\text{Co}^{\text{I}}(\text{chel})$ nucleophiles is the electrochemical reduction of $\text{Co}^{\text{III}}(\text{chel})$ using controlled potential electrolysis (26). This method provides a clean route to $\text{Co}^{\text{I}}(\text{chel})$ and has the advantage of selectivity

over the more commonly employed chemical methods since the reduction of the cobalt species to Co^0 or the reduction of the ligand can be avoided.

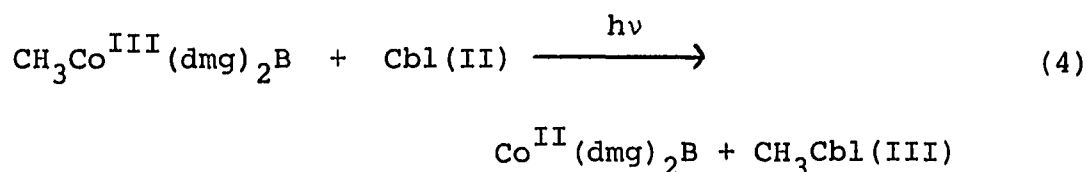
The use of $\text{Co}^{\text{I}}(\text{chel})$ nucleophiles in the synthesis of mono-alkylcobalt chelates has been very successful in the past, and more recently in the synthesis of complexes like $\text{RCo}(\text{BDM1,3pn})^+$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7$ and $\text{n-C}_4\text{H}_9$) (27); $\text{RCo}(\text{sal}_2\text{Bg})$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7$; $\text{Bg} = 1,2\text{-diiminoethane}, 1,2\text{-diiminopropane}, 1,2\text{-diimino-2-methylpropane}$ and $1,2\text{-diimino-o-phenylene}$); and $\text{RCo}(\text{sal}_2\text{cyclohex})$ ($\text{R} = \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7$) (28).

Organocobalt chelates can also be prepared by reacting $\text{Co}(\text{III})$ complexes directly with nucleophilic agents such as organolithium or Grignard reagents exemplified by (Eqn. 3) (16). This method is of general

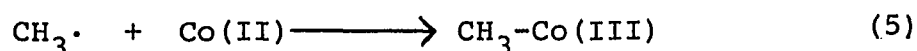


applicability and has considerable utility as a route to organocobalt chelates. Generally an excess of RMgX or RLi is employed in order to account for the reaction of these reagents with acidic protons which are often found on the chelating ligands.

The third general method of forming cobalt-carbon bonds involves the reaction of Co(II) chelates with organic radicals. For instance, Schrauzer et al. (29) synthesized methylcobalamin by the photolysis of methylcobaloxime under nitrogen in the presence of Cob(II)alamin (Eqn. 4). Similarly, heating a solution containing



^{14}C -methylcobalamin and ^{12}C -methylcobinamide in an atmosphere of nitrogen resulted in the formation of ^{14}C -methylcobinamide (30). Presumably both reactions involve the homolytic cleavage of the cobalt-carbon bond followed by reaction of the methyl radical with the Co(II) complex (Eqn. 5), since methyl radicals are known to be produced

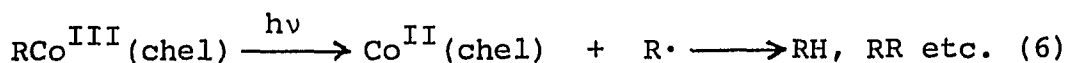


by the photolysis and thermolysis of methylcobalt complexes.

Cleavage of Cobalt-Carbon Bonds

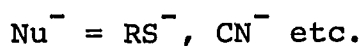
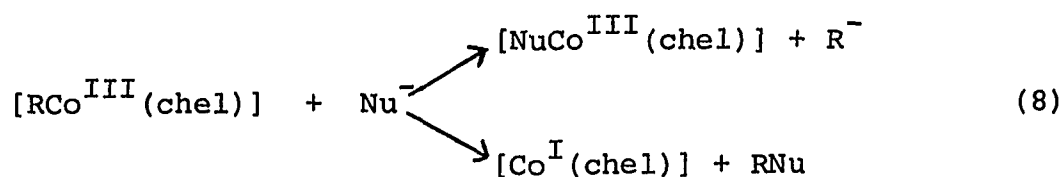
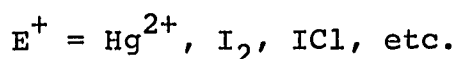
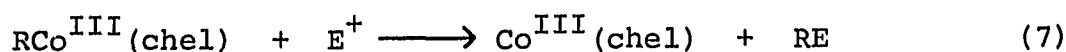
Cleavage of the cobalt-carbon bond of the mono-organocobalt complexes can occur by homolytic or heterolytic processes. Homolytic fission often occurs upon

irradiation of the complexes with light and leads to Co(II) complexes and an organic radical (Eqn. 6). The



radical may subsequently react by one of several routes:

(i) abstract a hydrogen atom from the ligand or solvent to form RH, (ii) dimerize to form RR, or (iii) lose a hydrogen atom to form C=C. Heterolytic cleavage can be induced by the reaction of the complexes with electrophiles or nucleophiles (Eqns. 7 and 8 respectively).



Electrophilic attack results in the formation of Co(III) complexes and carbanions, while nucleophilic attack results in the same products, or in some cases Co(I) complexes and carbonium ions. Often the intermediate reaction products can not be detected because they either undergo further reaction, or because the cleavage is concerted with attack of the reagent. In these cases evidence as to the mechanism of cleavage comes from kinetic measurements or the identification of the ultimate reaction products.

Individual complexes show surprising differences in their pattern of reactivity with respect to cobalt-carbon bond cleavage. The course and rates of these reactions depend not only on the nature of the organic ligand and attacking agent (if any), but also on the nature of the chelating ligand which plays an important role in the polarization of the cobalt-carbon bond. For example the order of chelating ligand donor power is $\text{sal}_2\text{en} > (\text{dmg})_2 > \text{BDM1,3pn}$ (23,31-33). As a consequence the $\text{RCo}(\text{sal}_2\text{en})$ complexes are more likely than $[\text{RCo}(\text{BDM1,3pn})]^+$ complexes to form carbanion intermediates.

Bis-Organocobalt Complexes

The remainder of this review will be concerned exclusively with the synthesis and reactivity of cobalt complexes containing two σ -bonded organo-ligands. Examples of complexes of this type are very limited in

contrast to the previously discussed mono-organocobalt chelates; and this subject has not been reviewed previously. Included in this category are compounds containing tetradentate macrocycles of the type $RR'Co(chel)$ (R and $R' = CH_3, C_2H_5, C_6H_5, C_6H_5CH_2$ etc.). These complexes differ from the mono-organocobalt chelates by the presence of a second σ -bonded organic ligand which occupies an axial position trans to the first. A second class of bis-organocobalt complexes which are of interest to this review includes the dialkyl and diaryl complexes which contain π -acceptor ligands, such as triphenylphosphine, 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), and acetylacetone (acac). These compounds are for the most part cis octahedral complexes, although other geometries are known. The structure and characterization of the bis-organocobalt complexes will be the subject of a subsequent section. Complexes of the type R_2Co ($R = C_6F_5, C_6H_5$) are known (34) but will not be discussed here since they are extremely unstable and not well characterized.

Preparation of Bis-organocobalt Complexes

Examples of bis-organocobalt chelates containing tetradentate macrocyclic ligands are few in number. In fact of all the macrocyclic ligands previously discussed only complexes of BDM1,3pn, tim, and CR are known (Fig. 5).

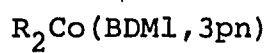
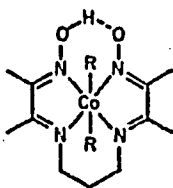
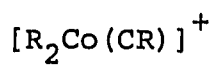
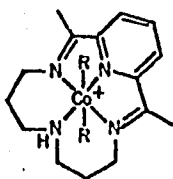
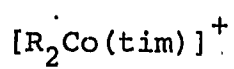
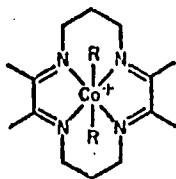


Fig. 5. General Structures of Bis-Organocobalt
Macrocyclic Complexes

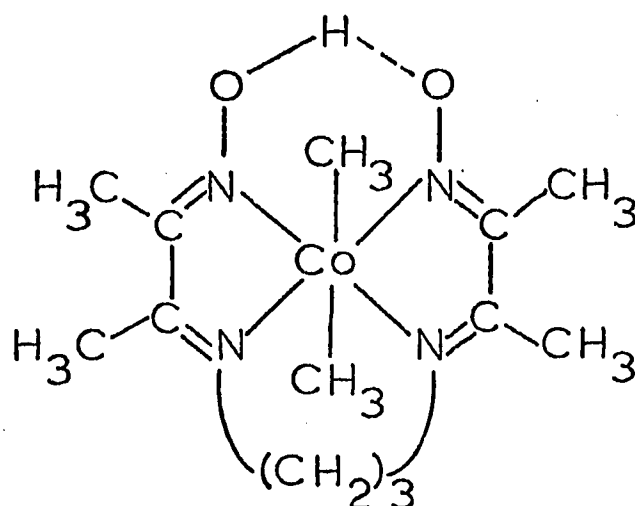


Figure 5a. Structure of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$

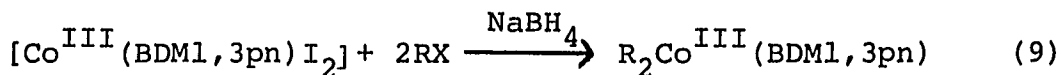
Complexes of the type $RR'Co(BDML,3pn)$ ($R = R' = CH_3$, $C_6H_5CH_2$) represents the first isolated examples (35), although Farmery and Busch (36) reported the isolation of $[(CH_3)_2Co(tim)]^+$ and $[(CH_3)_2Co(CR)]^+$ a short time later. Additional trans-dialkyl, trans-diaryl, and mixed alkyl-aryl complexes of these same ligands have been prepared, and their syntheses will now be discussed.

A survey of the literature reveals that two general procedures have been employed in the synthesis of these complexes. These include: (1) the reaction of Co(I) complexes with electrophiles, and (2) the reaction of Co(III) complexes with nucleophiles. In contrast to the mono-organocobalt chelates no examples of reactions of Co(II) complexes with radicals have been reported.

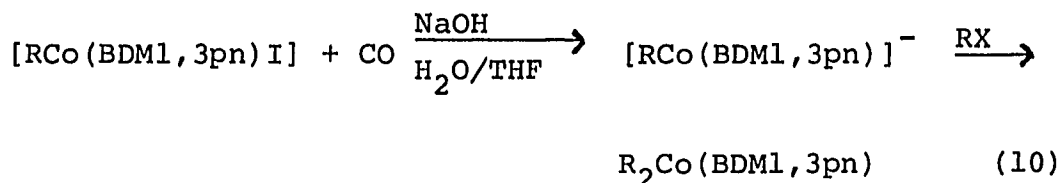
The formation of trans-dialkylcobalt complexes by method (1) implies the existence of intermediate nucleophiles of the type $RCo^I(chel)$. These intermediates can either be generated in situ or in some cases isolated in an oxygen-free atmosphere. The subsequent reaction of these species with alkyl halides affords the bis-organometallic compounds.

Costa et al. (35,37,38) synthesized complexes of the type $RR'Co(BDML,3pn)$ ($R = R' = CH_3$ or $C_6H_5CH_2$; $R = CH_3$, $R' = C_6H_5$) using variations of this method. The reaction of $[Co(BDML,3pn)I_2]$ with sodium borohydride in methanol in the presence of excess methyl iodide or benzyl chloride gave $(CH_3)_2Co(BDML,3pn)$ and $(C_7H_7)_2Co(BDML,3pn)$,

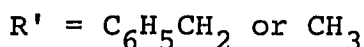
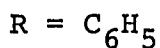
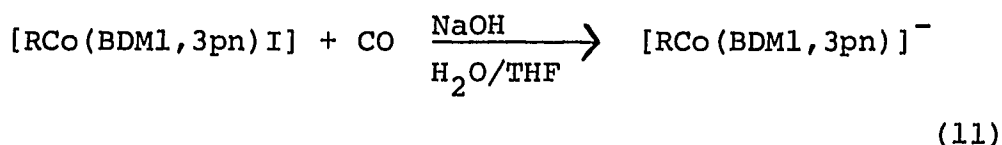
together with the mono-substituted derivatives $[\text{RCo}(\text{BDMl},3\text{pn})\text{I}]$ (Eqn. 9).



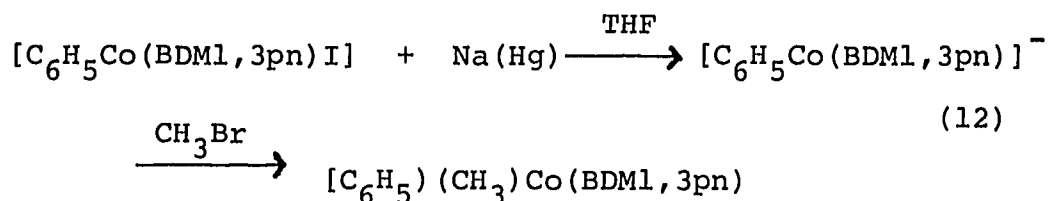
The dimethyl and dibenzyl complexes were also prepared by the carbon monoxide reduction of the corresponding mono-substituted derivatives (35,37). The reaction of $[\text{CH}_3\text{Co}(\text{BDMl},3\text{pn})\text{I}]$ or $[\text{C}_7\text{H}_7\text{Co}(\text{BDMl},3\text{pn})\text{I}]$ with CO in basic aqueous-THF gave a green solution. This color is characteristic of other Co(I) complexes (39) and is presumably $[\text{RCo}^{\text{I}}(\text{BDMl},3\text{pn})]^-$. The bis-organometallic derivatives are formed upon addition of the appropriate alkyl halide (Eqn. 10).



The existence of the assumed $[\text{RCo}(\text{BDMl},3\text{pn})]^-$ intermediates is proven by the formation of unsymmetrical bis-organometallic derivatives. For example the mixed methyl-phenyl and benzyl-phenyl derivatives were prepared by the CO reduction of $[\text{C}_6\text{H}_5\text{Co}(\text{BDMl},3\text{pn})\text{I}]$ in the presence of methyl iodide or benzyl chloride (35,37) (Eqn. 11).



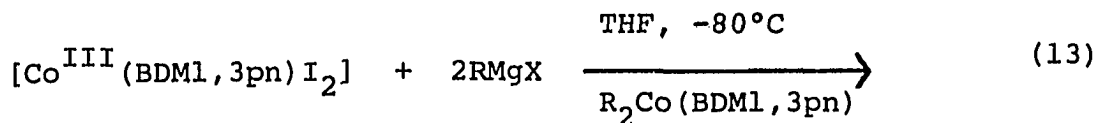
The methyl-phenyl complex was also prepared by employing sodium amalgam as the reducing agent in anhydrous THF, followed by the addition of methyl bromide (35) (Eqn. 12).



Schrauzer, Seck and Beckham (31) synthesized the dimethyl derivative by reacting the free ligand with cobalt acetate in methanol followed by NaBH_4 reduction in the presence of excess methyl iodide. After a reaction time of approximately 20 minutes the methanol solution was diluted with water in order to precipitate the neutral product. This in situ preparation has the advantage of not requiring the isolation of a $[\text{Co}(\text{BDML}, 3\text{pn})\text{X}_2]$ precursor, however it is of little use in the syntheses of the unsymmetrical derivatives.

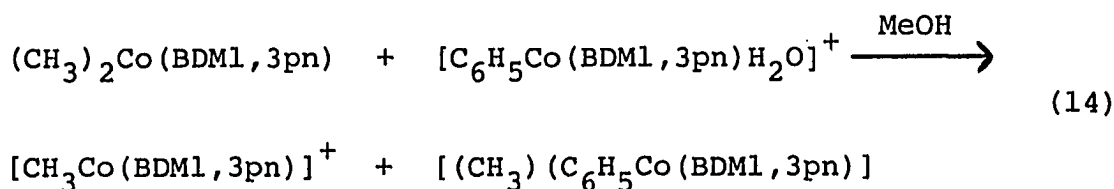
Farmery and Busch (32,33,36) synthesized compounds of the type $[RR'Co(CR)]^+Y^-$ and $[RR'Co(tim)]^+Y^-$ ($R = R' = CH_3$ or $C_6H_5CH_2$; $R = CH_3$, $R' = C_6H_5CH_2$; $Y = BPh_4^-$, PF_6^-) by the reactions of isolated $[RCo^I(CR)]$ and $[RCo^I(tim)]$ complexes with the appropriate alkyl halides. The trans-dialkylcobalt complexes were obtained as bright red or orange-brown crystals upon addition of BPh_4^- or PF_6^- . Other examples of complexes synthesized by this method include $[(C_2H_5)_2Co(CR)]^+$ and $[(n-C_3H_7)_2Co(CR)]^+$ (40). These reactions are significant not only because they represent another route to trans-dialkylcobalt chelates, but also because they confirm that the previously postulated $RCo^I(chel)$ complexes are indeed intermediates in their synthesis.

The second general method of preparing $RR'Co(chel)$ complexes is the reaction of $Co(III)$ complexes with Grignard reagents (method 2). For example, treatment of a suspension of $[Co(BDML,3pn)I_2]$ or $[Co(BDML,3pn)Br_2]$ in anhydrous THF with excess $RMgX$ ($R = CH_3$, C_6H_5 or $C_6H_5CH_2$) afforded an orange solution at $-80^\circ C$. Subsequent hydrolysis and concentration of these solutions resulted in the corresponding bis-organometallic derivatives $(CH_3)_2Co(BDML,3pn)$, $(C_6H_5)_2Co(BDML,3pn)$ and $(C_7H_7)_2Co(BDML,3pn)$ (eqn. 13). Presumably the trans-diphenyl complexes of

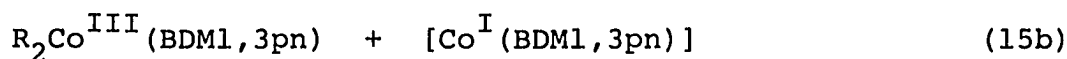
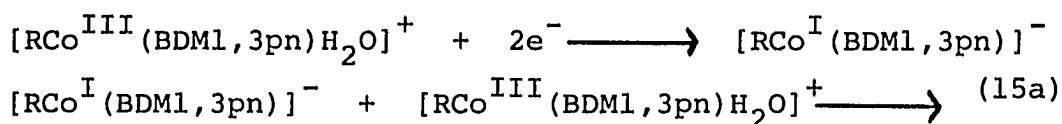


tim and CR could be prepared in this manner, but their synthesis has not been reported as of this writing. Other trans-diaryl complexes of the type $[(p\text{-FC}_6\text{H}_4)_2\text{Co}(\text{BDML}, 3\text{pn})]$ and $[(m\text{-FC}_6\text{H}_4)_2\text{Co}(\text{BDML}, 3\text{pn})]$ have been reported (41), but the method of preparation was not discussed.

The transfer of alkyl groups from one organo-cobalt complex to another represents a special case of method 2. Both the $[\text{RCo}(\text{BDML}, 3\text{pn})]^-$ anion and $(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$ have been used as alkylating agents. For example, when the dimethyl derivative is reacted in methanol or aqueous-THF with an equimolar amount of $[\text{C}_6\text{H}_5\text{Co}(\text{BDML}, 3\text{pn})\text{H}_2\text{O}]^+$, the mixed methyl phenyl derivative is obtained (42) (Eqn. 14).

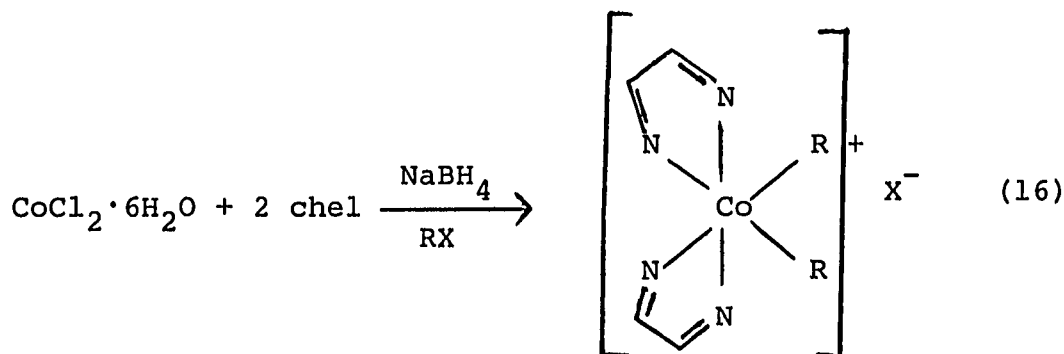


Similarly, the chemical or electrochemical reduction of $[\text{RCo}(\text{BDML},3\text{pn})\text{H}_2\text{O}]^+$ in air-free aprotic solvents yields the corresponding $[\text{RCo}(\text{BDML},3\text{pn})]^-$ anions, which behave as alkylating agents toward the $\text{Co}(\text{III})$ starting complexes (39,43,44). When $\text{R} = \text{methyl}$ or ethyl the trans- dialkylcobalt complexes $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ and $(\text{C}_2\text{H}_5)_2\text{Co}(\text{BDML},3\text{pn})$ are isolated (Eqn. 15). This reac-



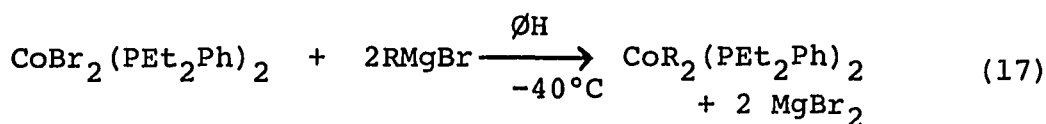
tion has been interpreted in terms of a carbanion transfer from the $\text{Co}(\text{I})$ to the $\text{Co}(\text{III})$ complex, however, a carbonium ion transfer from the $\text{Co}(\text{III})$ to the $\text{Co}(\text{I})$ complex can not be ruled out.

In contrast to the bis-organometallic complexes containing macrocyclic ligands cis- dialkyl complexes are not generally synthesized by oxidative addition of alkyl halides and $\text{Co}(\text{I})$ nucleophiles. However, Mestroni et al. (45) prepared a series of stable dialkyl cobalt complexes of 2,2'-bipyridine and 1,10-phenanthroline using this method. The sodium borohydride reduction of methanolic solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of bipy or phen and alkylhalides gave the complexes I-VI after adding the appropriate anion (Eqn. 16).



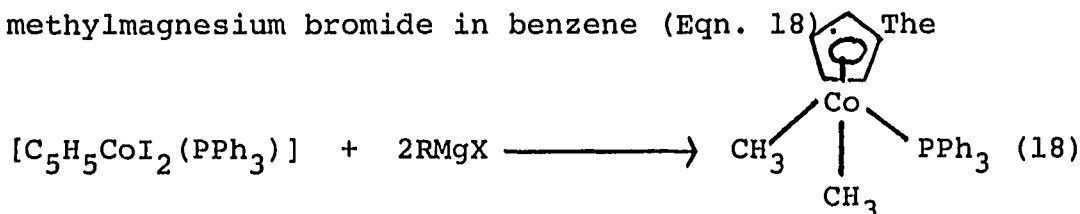
- I $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$, $\text{X} = \text{I}^-$, $\text{chel} = \text{bipy}$
 II $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$, $\text{X} = \text{ClO}_4^-$, $\text{chel} = \text{bipy}$
 III $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$, $\text{X} = \text{PF}_6^-$, $\text{chel} = \text{bipy}$
 IV $\text{R} = \text{CH}_3$, $\text{X} = \text{ClO}_4^-$, $\text{chel} = \text{bipy}$
 V $\text{R} = \text{C}_2\text{H}_5$, $\text{X} = \text{ClO}_4^-$, $\text{chel} = \text{bipy}$
 VI $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$, $\text{X} = \text{I}$, $\text{chel} = \text{phen}$

The majority of the known non-macrocyclic dialkyl and diarylcobalt complexes have been synthesized using Grignard or organolithium reagents. This method was first successfully employed by Chatt and Shaw (46) in the synthesis of diarylcobalt(II) complexes of the type $\text{R}_2\text{Co}(\text{PR}'_3)_2$ ($\text{R} = \text{mesityl}$, 2-biphenyl, 2-methyl-1-naphthyl, pentachlorophenyl; $\text{PR}'_3 = \text{PEt}_2\text{Ph}$). In general these organometallic complexes were prepared by the reaction of the appropriate Grignard reagent or organolithium reagent with a phosphine metal halide complex in benzene at -40°C (Eqn. 17). In most cases the organolithi-



um reagents resulted in poorer yields. The preparation of similar alkylcobalt(II) derivatives was attempted by the same methods but no dialkyl compounds were isolated.

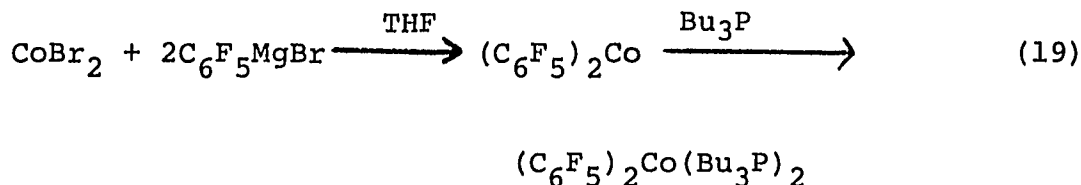
Yamazaki and Hagihara (47) subsequently reported that dialkylcobalt(II) complexes of π -cyclopentadienyl and tertiary phosphines could be prepared by the Grignard method. Stable σ -bonded dialkyl complexes of the type $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{C}_7\text{H}_7)_2\text{PPh}_3]$ and $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{CH}_3)_2\text{PPh}_3]$ were obtained by treatment of a slurry of the iodide, $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{I})_2\text{PPh}_3]$, with benzylmagnesium chloride or methylmagnesium bromide in benzene (Eqn. 18). The



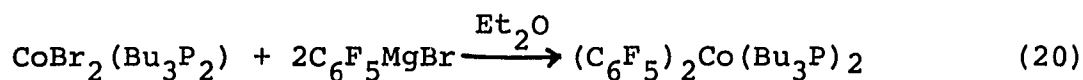
orange-red complexes were isolated in 20% yield after hydrolysis of the mixture with water. The corresponding monoalkyl products, $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{R})(\text{PPh}_3)]$, were also isolated, and presumably account for the low yields of the dialkyl complexes. King (48) also reported the synthesis of the dimethyl complex by the same method. The mixed methyl-benzyl complex was prepared by the reaction of $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{CH}_3)(\text{I})(\text{PPh}_3)]$ with benzylmagnesium chloride. This complex represents the first isolated example of a cobalt complex containing two different alkyl groups.

An attempt to prepare stable dimethyl cobalt(II) complexes using a series of substituted pyridines as stabilizing ligands was somewhat successful (49). The complexes were formed in situ by the reaction of $\text{CoCl}_2 \cdot (\text{Py})_2$ with methyl-magnesium bromide in benzene, however, all efforts to isolate the products resulted in their decomposition. The complexes were characterized by electron paramagnetic resonance spectroscopy at -130°C but no details were given.

The stable phosphine complex bis(tri-n-butylphosphine)bis(pentafluorophenyl)cobalt(II), $\text{Co}(\text{C}_6\text{F}_5)_2(\text{Bu}_3\text{P})_2$, was obtained by the reaction of pentafluorophenylmagnesium bromide and cobalt(II) bromide in THF, followed by the addition of tri-n-butylphosphine (34) (Eqn. 19). This

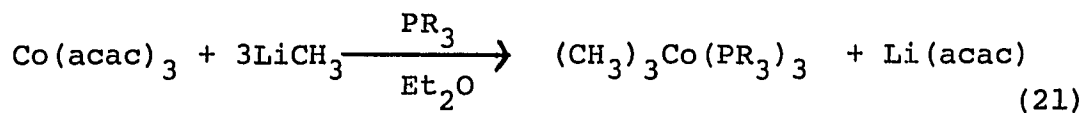


complex was also prepared by the method of Phillips (50) through the reaction of $\text{C}_6\text{F}_5\text{MgBr}$ and $\text{CoBr}_2(\text{Bu}_3\text{P})_2$ in ether (Eqn. 20).

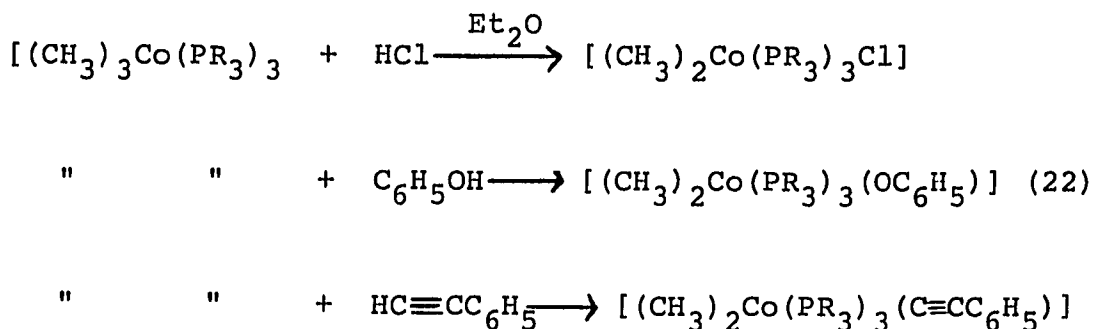


Two recent papers by Klein and Karsch describe the synthesis of novel trimethylcobalt(III), dimethylcobalt(III), and dimethylcobalt(II) complexes of trimethylphosphine (51,52). The trimethylcobalt(III) complex, trimethyltris(trimethylphosphine)cobalt(III) is of particular interest since it represents the first example of a stable trialkylcobalt complex. In addition, it readily undergoes reactions with compounds containing acidic hydrogens yielding the corresponding dimethylcobalt(III) derivatives and methane.

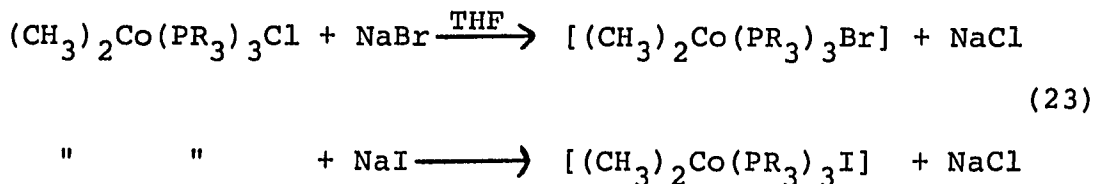
The synthesis of $(\text{CH}_3)_3\text{Co}(\text{PR}_3)_3$ ($\text{R} = \text{CH}_3$), involves the reaction at -70°C of $\text{Co}(\text{acac})_3$ and three equivalents of methyllithium, in the presence of an excess of trimethylphosphine in ether. After slowly warming the solution to 20°C the product is precipitated with pentane (Eqn. 21).



The dimethylcobalt(III) complexes of the type $[(\text{CH}_3)_2\text{Co}(\text{PR}_3)_3\text{X}]$ ($\text{X} = \text{Cl}^-$, $^-\text{OC}_6\text{H}_5$, $^-\text{C} \text{CC}_6\text{H}_5$) were prepared by the reaction of the trimethyl complex with HCl, phenol, and phenylacetylene (Eqn. 22). Additional

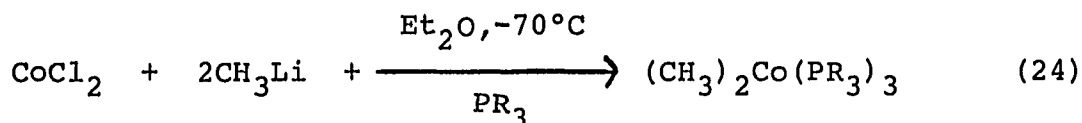


dimethylcobalt complexes were obtained by the displacement of Cl^- from $(\text{CH}_3)_3\text{Co}(\text{PR}_3)_3\text{Cl}$ by Br^- and I^- (Eqn. 23).



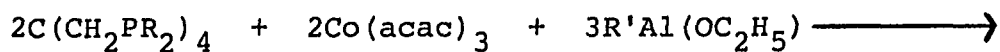
The five-coordinate dimethylcobalt(II) complex dimethyltris(trimethylphosphine)cobalt(II) $(\text{CH}_3)_2\text{Co}-(\text{CH}_3)_3\text{P})_3$ was prepared under a nitrogen atmosphere from cobalt chloride and methyllithium in the presence of an excess of trimethylphosphine. After one hour the ether solution was slowly warmed from -70°C to $+20^\circ\text{C}$ and the solution evaporated to dryness in vacuo. The residue was extracted with pentane and the product precipitated at

-40°C (Eqn. 24).

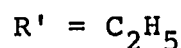
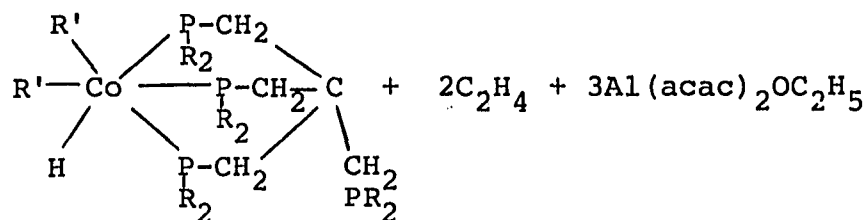


The employment of organoaluminum compounds in combination with $\text{Co}(\text{acac})_3$ in the presence of π -acceptor ligands provides a very convenient route to the preparation of cis-dialkyl cobalt complexes. It is assumed that these alkylation reactions proceed through stepwise exchange reactions of the acac ligands of $\text{Co}(\text{acac})_3$ with the alkyl groups of the alkylaluminum compounds; resulting in intermediate complexes having both alkyl and acac ligands. For example, Yamamoto et al. (53) prepared diethylbis(bipyridyl)cobalt, $(\text{C}_2\text{H}_5)_2\text{Co}(\text{bipy})_2$, by the reaction of $\text{Co}(\text{acac})_3$, 2,2'-dipyridine, and diethylaluminum monoethoxide in ether at -10°C. The yield based on $\text{Co}(\text{acac})_3$ was 85%.

A similar reaction of $\text{Co}(\text{acac})_3$ with diethylaluminum monoethoxide in the presence of tetrakis(diphenylphosphinomethyl)methane results in the formation of an air sensitive cis-diethylcobalt complex (54) (Eqn. 25).

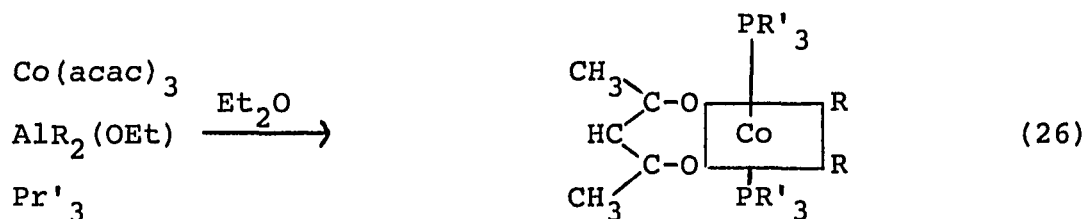


(25)



The composition and structure of the 4-(diphenylphosphinomethyl)-1,1-diethyl-1-hydrido-2,2,6,6,7,7-hexaphenyl-2,6,7-triphospha-1-cobaltabicyclo [2.2.2]-octane complex was determined by elemental analysis, cryoscopic molecular weight determination and infrared spectroscopy.

Finally, in a very recent paper Ikariya and Yamamoto (55) described the synthesis and properties of a series of trivalent cis-dialkylcobalt complexes with acetylacetonato and tertiary phosphine ligands. These complexes were also prepared using dialkylaluminum monoethoxide reagents. Upon mixing $\text{Co}(\text{acac})_3$, tertiary phosphine, and the appropriate dialkylaluminum reactants in ether, the complexes I-V were obtained (Eqn. 26).



I	R = Me,	PR' ₃ = PEt ₃
II _a	R = Me,	PR' ₃ = PPhMe ₂
II _b	= Et,	" = "
II _c	= <u>n</u> -Pr,	" = "
II _d	= <u>i</u> -Bu,	" = "
III	R = Me,	PR' ₃ = PPh ₂ Me
IV	R = Me,	PR' ₃ = P(<u>n</u> -Bu) ₃
V	R = Et-d ₃ ,	PR' ₃ = PPhMe ₂

Physical Properties

The structures and physical properties of the bis-organometallic compounds have been established in most cases utilizing the usual techniques of X-ray analysis, NMR and IR spectroscopy, chemical analysis and magnetic susceptibility measurements. Although the characterization of the bis-organocobalt macrocyclic compounds are of greatest interest to this work, the properties of the non-macrocyclic complexes will also be discussed.

Recently the crystal and molecular structure of one of the macrocyclic compounds, $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ was determined by X-ray analysis (56) (Fig. 5). The structure was solved using the heavy atom method and the results confirm the trans configuration of the methyl groups, and a distorted octahedral geometry about the cobalt atom. In analogy to the mono-organocobalt chelates, the four nitrogen atoms of the macrocyclic ligand occupy the equatorial positions and are coplanar within experimental error. The cobalt atom is displaced only 0.029\AA from the plane defined by the four nitrogen atoms. The six-membered ring containing the cobalt atom, imine nitrogens, and methylene bridge has a flattened chair conformation with the central methylene group of the bridge displaced 0.78\AA above the plane. The mean values of the four $\text{C}-\text{CH}_3$ bond lengths (1.506\AA) is in agreement with the expected value (57); however, the shorter than expected $\text{N}-\text{C}$ (1.338\AA) and $\text{C}-\text{C}$ (1.309\AA) bond lengths indicate extended π -delocalization in the two five-membered rings. This compares to mean $\text{N}-\text{C}$ and $\text{C}-\text{C}$ bond lengths of 1.29\AA and 1.47\AA respectively in $\text{RCo}(\text{dmg})_2$ complexes (58) indicating less delocalization.

The two axial cobalt-carbon bond lengths are equal and have a mean value of 2.047\AA . These values compare favorably with other methyl cobalt chelates and

are only slightly longer than the value of 1.99\AA found for the corresponding monomethyl complex $[\text{CH}_3\text{Co}-(\text{BDML},3\text{pn})\text{H}_2\text{O}]^+$ (59). The N-Co-CH₃ bond angles of 89.7° indicates a nearly perpendicular orientation of the axial methyl groups with respect to the macrocyclic ligand plane.

The molecular structure of one non-macrocyclic complex was also determined by X-ray analysis. Owsten and Rowe (60) confirmed the previously assumed (46) trans-square planar geometry of dimesitylbis(diethylphenylphosphine)cobalt(II), $\text{Co}(\text{mesityl})_2(\text{P}(\text{C}_2\text{H}_5)_2\text{Ph})_2$, which was based on dipole moment and magnetic susceptibility measurements. The planes of the mesityl groups are perpendicular to the plane of the complex, a consequence of the ortho-methyl substituents. This geometry is unusual in complexes of Co(II) and it is presumably a consequence of the large ligand field strength of the phosphines, and steric factors which force a planar configuration of the ligands.

The majority of the bis-organometallic compounds are diamagnetic Co(III) complexes, and as a consequence useful NMR spectra have been obtained. The ^1H , ^{31}P and ^{19}F spectra have been used to characterize the structure and electronic distribution of the complexes. Some of the more interesting results will be discussed.

The ^1H NMR spectra of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ and $[(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Co}(\text{BDML},3\text{pn})]$ in CDCl_3 (61); and of $[(\text{CH}_3)_2\text{Co}(\text{tim})\text{BPh}_4]$ and $[(\text{CH}_3)_2\text{Co}(\text{CR})]\text{BPh}_4$ in $(\text{CD}_3)_2\text{SO}_4$ (33) have been reported. The spectra confirm the presence of two axial organo groups attached to cobalt (Table I). The high field position of these methyl groups is common for dimethylcobalt complexes and reflects the well-known electron donating capability of CH_3^- (34,62,63) thus the buildup of charge density on cobalt. This effect is further demonstrated in the series of complexes of the type $[(\text{CH}_3)(\text{X})\text{Co}(\text{BDML},3\text{pn})]$ ($\text{X} = \text{I}, m\text{-C}_6\text{H}_4, p\text{-FC}_6\text{H}_4, \text{C}_6\text{H}_5, \text{CH}_3$) (Table I), where the axial methyl chemical shift moves to higher field in the order $\text{I} < m\text{-FC}_6\text{H}_4 < p\text{-FC}_6\text{H}_4 < \text{C}_6\text{H}_5 < \text{CH}_3$. The superior σ -donor power of CH_3^- found in this study is in agreement with a similar investigation of the ^{19}F NMR spectra of substituted $[(\text{FC}_6\text{H}_5)\text{Co}(\text{BDML},3\text{pn})\text{X}]$ complexes (41).

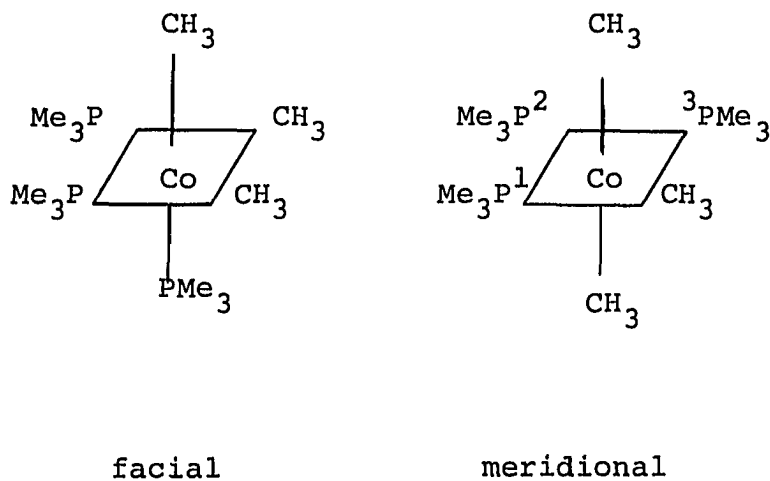
Klein and Karsch (51) demonstrated the usefulness of ^{31}P NMR spectra in the determination of the structure of $[(\text{CH}_3)_3\text{Co}(\text{PR}_3)_3]$. Both the facial and meridional isomers are possible. The facial isomer has three equivalent phosphorous atoms, and should therefore produce only one peak in the ^{31}P NMR spectrum. The meridional isomer has two equivalent phosphorous atoms

Table I. ^1H -NMR Spectra of $\text{CH}_3\text{Co}(\text{chel})\text{X}$ Complexes

$\text{CH}_3\text{Co}(\text{BDML}, 3\text{pn})\text{X}$	X	$\text{Co}-\text{CH}_3^{\text{a}}$	$\text{C}-\text{CH}_3^{\text{b}}$	$\text{N}-\text{CH}_2^{\text{b}}$	$\text{C}-\text{CH}_2-\text{C}^{\text{b}}$
	CH_3	0.06 (2)	2.19, 2.22	3.68	-
	C_6H_5	0.35 (1)	2.32	3.56	1.89
	$\text{p-FC}_6\text{H}_4$	0.36 (1)	2.31	3.53	-
	$\text{m-FC}_6\text{H}_4$	0.38 (1)	2.32	3.56	-
	I	0.71 (1)	2.24, 2.30	-	-
$[\text{CH}_3\text{Co}(\text{tim})\text{X}]\text{BPh}_4$	CH_3	0.36 (2)	-	-	-
$[(\text{CH}_3)\text{Co}(\text{CR})\text{X}]\text{BPh}_4$	CH_3	0.18 (2)	-	-	-

^a() Refers to number of equivalent ligands on cobalt.

^bChemical shifts not reported or not applicable.



(P₁, P₃), and a different third phosphorus atom (P₂). This compound should give rise to two peaks of 2:1 intensity. The spectrum actually observed consisted of a doublet and an upfield triplet of 2:1 intensity ratio, thus confirming the meridional structure. Unfortunately, the five-coordinate complex dimethyl tris-(tri-methylphosphine)cobalt(II) could not be characterized by ³¹P or ¹H NMR (52), presumably because of its paramagnetism.

The ¹H and ³¹P NMR spectra of the dialkylcobalt complexes CoR₂(acac)(PR'₃)₂ discussed earlier confirm that these compounds have an octahedral configuration with the two cobalt-bonded alkyl groups cis to each other (55) (see Eqn. 26). The methyl protons of acac are magnetically equivalent and appear as a singlet from

-80 to +20°C. The protons in the two cobalt-bonded methyl groups are also equivalent and appear as a triplet due to coupling with ^{31}P . The ^{31}P NMR spectra of these complexes indicate that the two equivalent phosphorous nuclei undergo exchange at room temperature since the singlet observed at -70°C broadens considerably as the temperature is raised.

Infrared spectroscopy has not been utilized extensively in the characterization of the bis-organocobalt complexes as of this writing. However, the frequencies $\nu(\text{Co-CH}_3)$ and $\delta_s(\text{Co-CH}_3)$ have been reported for several dimethyl complexes (51,52, 55). Although correlation of the existing data is difficult due to the different matrices used, several trends are apparent. For example, the $\nu(\text{Co-CH}_3)$ and $\delta_s(\text{Co-CH}_3)$ frequencies are found in the regions 460-479 cm^{-1} and 1157-1161 cm^{-1} respectively for the series of complexes $[(\text{CH}_3)_2\text{Co}(\text{PR}_3)_2\text{X}]$ ($\text{X} = \text{CH}_3, \text{Cl}, \text{Br}, \text{I}$) (51). The order of increasing frequency $\text{CH}_3 < \text{I} < \text{Br} < \text{Cl}$ was observed for $\nu(\text{Co-CH}_3)$. Other dialkyl complexes of the type $[\text{R}_2\text{Co}(\text{acac})(\text{PR}'_3)_2]$ show $\nu(\text{Co-C})$ bands at a slightly higher frequency (570-585 cm^{-1}) (55).

Reactions

The intent of this section is to survey the chemical reactions of the bis-organocobalt compounds. In contrast to the mono-organometallic compounds very little

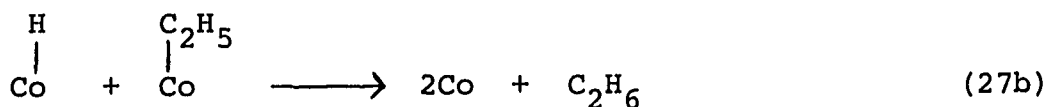
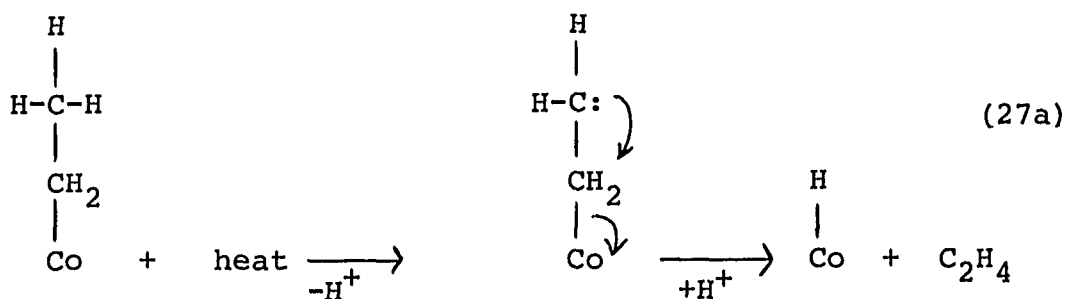
work has been done on the reactivity of these complexes. Generally, reactions occur with cleavage of a cobalt-carbon bond, however simple substitution reactions involving other ligands are known. This discussion will be classified where possible in terms of the type of attacking reagent (if any), and the sites at which reaction may occur.

Reactions with Light and Heat. In analogy to the mono-organocobalt complexes cobalt-carbon bond cleavage may be induced photochemically or thermally in both the solid state and in solution. The photo- and thermal lability of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ was studied in detail by Witman and Weber (64), and evidence was presented for a homolytic process. These results will be discussed in a later section. The closely related complexes $[(\text{CH}_3)_2\text{Co}(\text{tim})]^+$ and $[(\text{CH}_3)_2\text{Co}(\text{CR})]^+$ are also reportedly light sensitive in solution (32), but details of these reactions were not discussed.

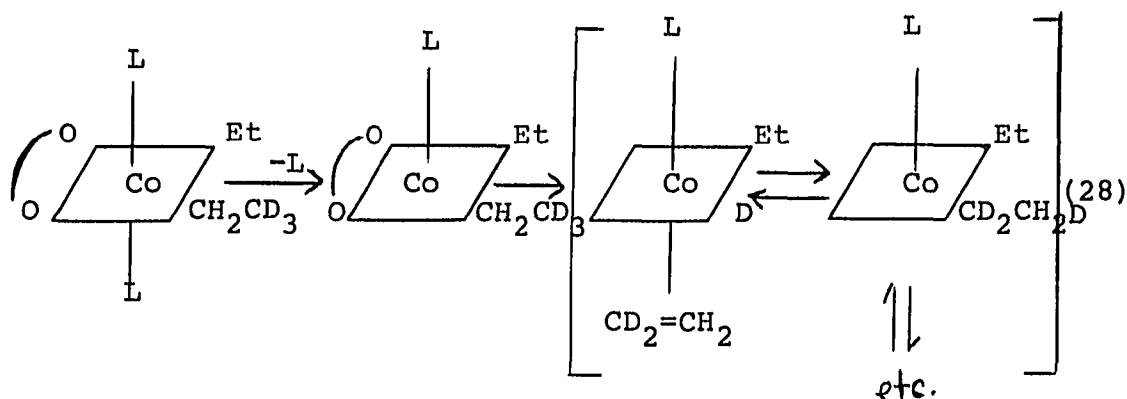
Several papers have been published on the thermal decomposition reactions of dialkylcobalt complexes, and mechanisms involving both the homolytic scission of cobalt-carbon σ -bonds, and the β -elimination of cobalt hydrides have been proposed (54,55,64). The latter course has been established for the cis-diethyl complexes $(\text{C}_2\text{H}_5)_2\text{Co}(\text{acac})(\text{PR}'_3)_2$ ($\text{PR}'_3 = \text{PPhMe}_2$) (55), and $\text{H}(\text{C}_2\text{H}_5)_2\text{Co}(\text{PCH}_2\text{Ph}_2)_4\text{C}$ (54).

On heating these complexes in the solid state ethylene and ethane are formed in a 1:1 ratio. The observation that n-butane is not formed in these reactions precludes the possibility that ethane and ethylene are formed by the disproportionation of free ethyl radicals; since the rate constant for the coupling of ethyl radicals is greater than that for their disproportionation by a factor of 6 (65).

Further evidence supporting the contention that ethyl radicals are not intermediates was provided from experiments using $(\text{CD}_3\text{CH}_2)_2\text{Co}(\text{acac})(\text{PR}'_3)_2$ (55). The formation of $\text{CH}_2=\text{CD}_2$ and CH_2DCD_3 in a 1:1 molar ratio upon heating is compatible with a mechanism involving the elimination of a cobalt hydride and concomitant formation of 1 equivalent of ethylene; followed by reduction of a second cobalt-alkyl bond by the hydride to yield 1 equivalent of ethane (Eqn. 27).



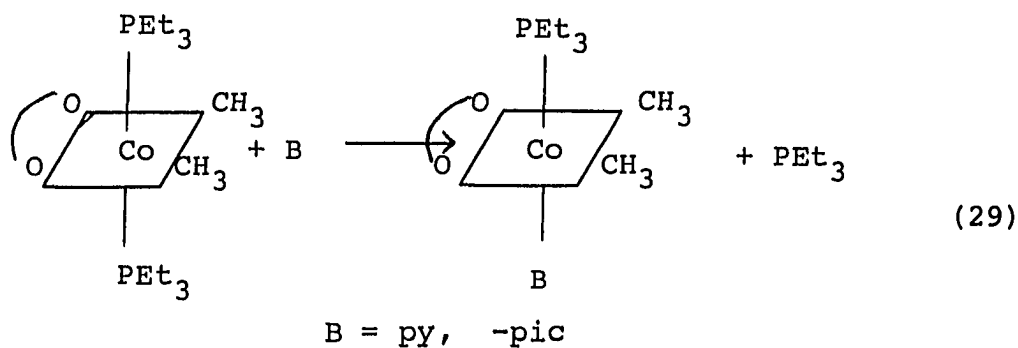
In addition, the solution thermolysis of $(\text{CD}_3\text{CH}_2)_2\text{Co}-(\text{acac})(\text{PR}'_3)_2$ gave appreciable quantities of cis- and trans- $\text{C}_2\text{H}_2\text{D}_2$, C_2HD_3 and $\text{C}_2\text{H}_3\text{D}$. These products are the result of a H-D scrambling process, and can be accounted for by the reversible elimination, ethylene-insertion process shown below (Eqn. 28).



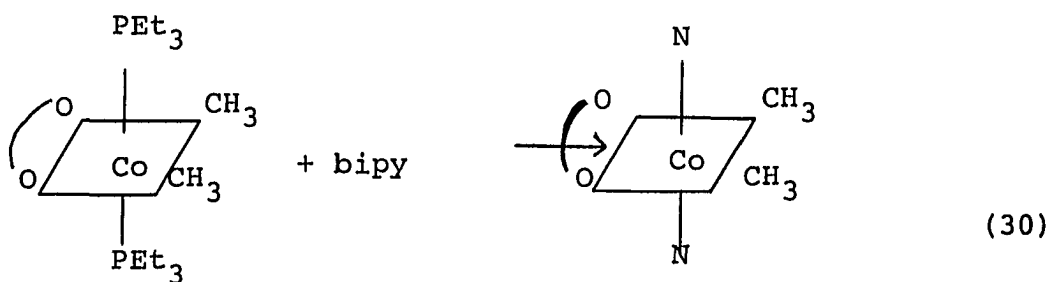
Substitution Reactions. A few of the non-macrocyclic bis-organometallic compounds undergo a variety of substitution reactions which do not affect their Co-C bonds. These reactions are unknown for the dialkyl and diaryl derivatives of the tetradentate ligands BDML₃pn₂tim, and CR; a consequence of the chelate effect, and of strong pi electron interactions between the metal ion and the imine and oxime nitrogens.

Yamamoto and Ikariya (55) observed that one of the tertiary phosphine ligands in $(\text{CH}_3)_2\text{Co}(\text{acac})(\text{PR}_3')_2$ could

be replaced by pyridine or δ -picoline to give $(\text{CH}_3)_2\text{Co}(\text{acac})(\text{PR}'_3)(\text{Py})$ and $(\text{CH}_3)_2\text{Co}(\text{acac})(\text{PR}_3')(\delta\text{-pic})$ respectively (Eqn. 29).

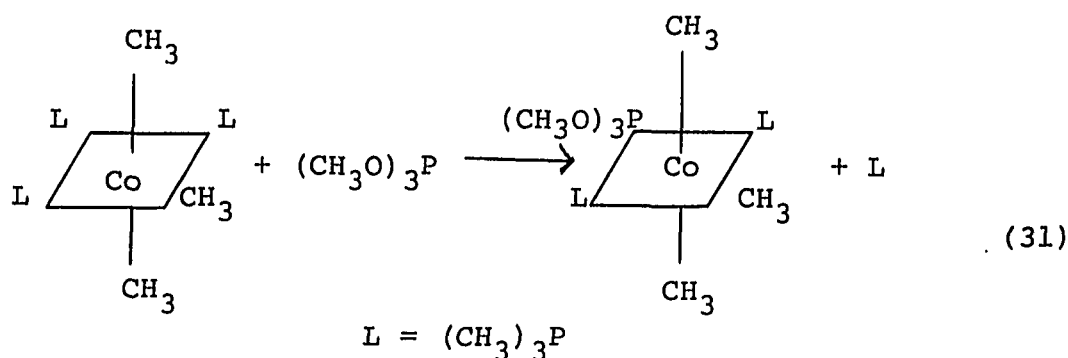


The two phosphine ligands were also replaced by the bidentate ligand 2,2'-bipyridine (bipy) to give $(\text{CH}_3)_2\text{Co}(\text{acac})(\text{bipy})$ (Eqn. 30). These results are in agreement



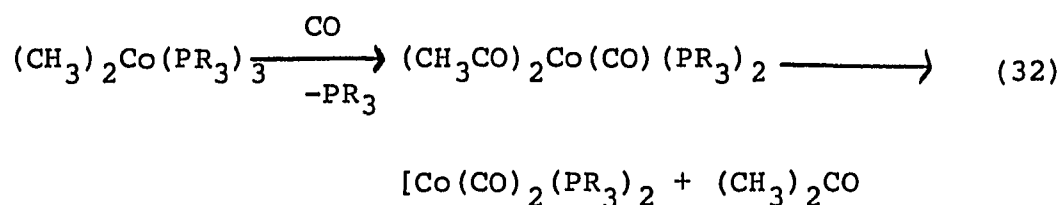
with the variable temperature ^{31}P NMR spectra of these complexes which indicate that rapid phosphine exchange occurs at room temperature (55).

Other complexes containing phosphine ligands react similarly. The dimethyl complex $(\text{CH}_3)_2\text{Co}(\text{PR}_3)_3\text{Cl}$ reacts with excess NaX ($\text{X} = \text{Br}^-$, I^-) to yield the corresponding bromide and iodide complexes. This reaction was discussed earlier with respect to its synthetic utility (51). In addition, trimethylphosphite selectively replaces the trimethylphosphine ligand which is trans to a CH_3 group, in its reaction with $(\text{CH}_3)_3\text{Co}(\text{PR}_3)_3$ (Eqn. 31). The stereospecificity of this reaction

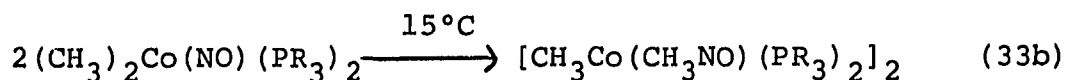
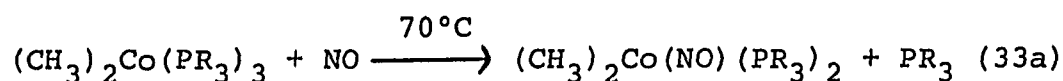


presumably reflects the well-known trans labilizing influence of CH_3 .

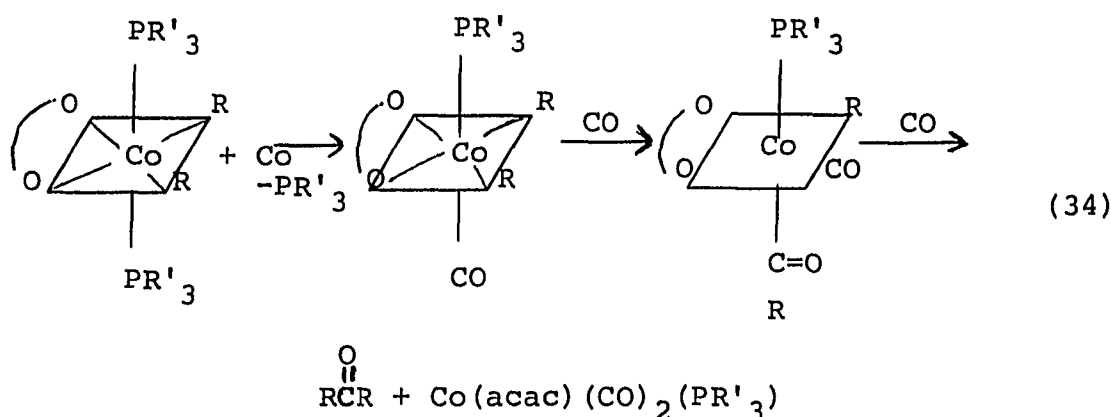
Insertion Reactions. Relatively few insertion reactions involving the Co-C bond of bis-organocobalt complexes are known. Solutions of $(\text{CH}_3)_2\text{Co}(\text{PR}_3)_3$ absorb carbon monoxide at 20°C to form acetone and diamagnetic $\text{Co}(0)$ dimers of the composition $[\text{Co}(\text{CO})_2(\text{PR}_3)_2]_2$ (52). The formation of intermediate σ -acetyl cobalt(II) complexes followed by the reductive elimination of acetone was assumed (Eqn. 32). The same dimethyl complex



reacts with NO at low temperature to form $(\text{CH}_3)_2\text{Co(NO)}-(\text{PR}_3)_2$ which rearranges via NO insertion into a Co-C σ -bond to give $[\text{CH}_3\text{Co}(\text{CH}_3\text{NO})(\text{PR}_3)_2]_2$ at 15°C (52) (Eqn. 33).

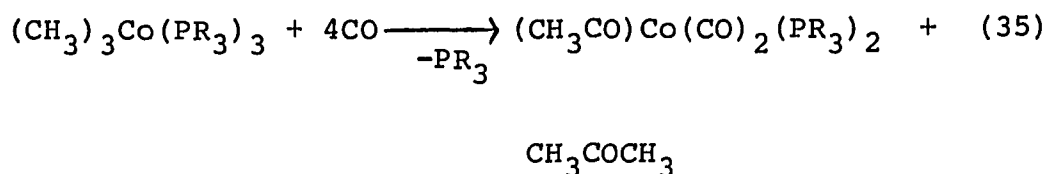


The dialkyl complexes $\text{R}_2\text{Co(acac)(PR}'_3)_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{i-C}_4\text{H}_9$; $\text{R}' = \text{C}_2\text{H}_5, \text{n-C}_4\text{H}_9$) react with carbon monoxide to yield the corresponding dialkyl ketones and $\text{Co}^{\text{I}}(\text{acac})(\text{CO})_2\text{PR}'_3$ (55) (Eqn. 34). Carbon



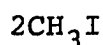
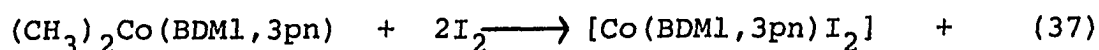
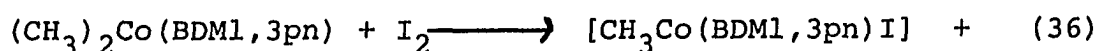
monoxide insertion into one of the alkylcobalt bonds followed by reductive elimination of the ketone was also assumed.

Finally, in support of the foregoing assumptions the trimethylcomplex $(\text{CH}_3)_3\text{Co}(\text{PR}_3)_3$ reacts with 4 equivalents of carbon monoxide to form the stable acetyl cobalt(I) complex $(\text{CH}_3\text{CO})\text{Co}(\text{CO})_2(\text{PR}_3)_2$ and acetone (51) (Eqn. 35).

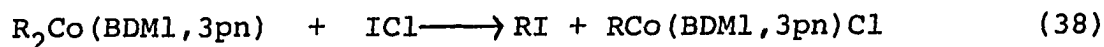


Reactions with Electrophiles. Electrophilic reagents that induce cleavage of cobalt-carbon bonds in these complexes include halogen molecules, H_3O^+ , and metal ions. Tauszher et al. (66) examined the reactions

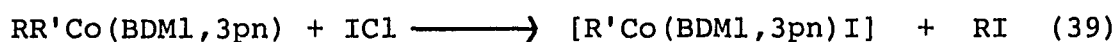
of halogens with $RR'Co(BDML,3pn)$ ($R = CH_3, C_2H_5, C_6H_5$; $R' = CH_3, C_6H_5$) in $CHCl_3$. The dealkylation (or dearylation) reactions of these complexes with I_2 are interesting since the reactions occur with two different stoichiometries depending upon the I_2 /complex molar ratio. These 1:1 and 2:1 reactions, exemplified by the dimethyl derivative, are shown in (Eqns. 36 and 37 respectively).



Information about the mechanism of these reactions was obtained using the polar ICl molecule in place of I_2 . When $R_2Co(BDML,3pn)$ ($R = CH_3, C_6H_5$) was treated with ICl in the molar ratio ICl /complex = 1, equation 38 was observed. The exclusive formation of RI in pre-



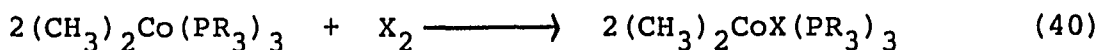
ference to RCl was interpreted in terms of an electrophilic attack at carbon by the electropositive I^+ species. Furthermore, the second cobalt-carbon bond was shown to be less easily cleaved, since the products R'I , $\text{RCo}(\text{BDML},3\text{pn})\text{Cl}$ and $[\text{Co}(\text{BDML},3\text{pn})(\text{H}_2\text{O})_2]^{2+}$ were not found in the reactions of $\text{RR'Co}(\text{BDML},3\text{pn})$ ($\text{R} = \text{CH}_3$, C_2H_5 ; $\text{R}' = \text{C}_6\text{H}_5$) with ICl (Eqn. 39). The preference for



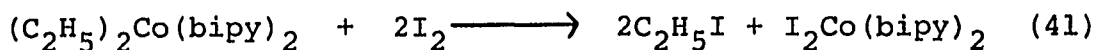
the alkyl substituent in the reactions of the unsymmetrical complexes was not expected since similar reactions involving the unsymmetrical organomercurials and iodine gave the opposite result (67). In addition, this behavior appears to be in contrast to kinetic data for the reactions of $\text{R}_2\text{Co}(\text{BDML},3\text{pn})$ with $\text{C}_6\text{H}_5\text{Hg}^+$ (40) and $\text{RCo}(\text{BDML},3\text{pn})$ with Hg^{2+} (68); where the phenyl derivatives react faster than the methyl derivatives. This anomaly has not been explained satisfactorily and more data is needed. The analogous bis-organocobalt macrocycles $[\text{RR'Co}(\text{tim})]^+$ and $[\text{RR'Co}(\text{CR})]^+$ should also react with halogens in similar fashion, but these reactions remain unstudied.

The manner in which divalent dialkylcobalt complexes react with halogens appears to be governed in some respects by the coordination number of the complex.

For example, the five-coordinate complexes $(\text{CH}_3)_2\text{Co}(\text{PR}_3)_3$ are rapidly oxidized by iodine or bromine to give the corresponding dimethylcobalt(III) halides (Eqn. 40),

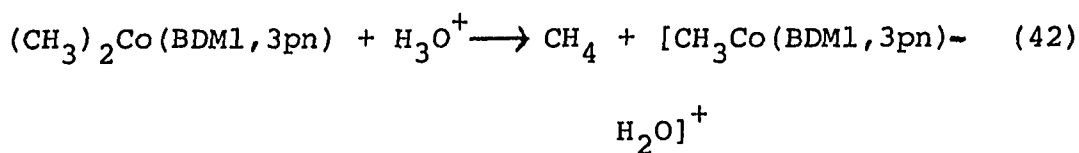


without cleavage of a cobalt-carbon bond (52). The octahedral complex $(\text{C}_2\text{H}_5)_2\text{Co}(\text{bipy})_2$, on the other hand, reacted with iodine to give ethyl iodide and the corresponding iodocomplex (53) (Eqn. 41).



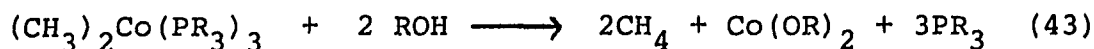
Nearly all of the bis-organocobalt complexes discussed in this review are susceptible to electrophilic attack by H_3O^+ . These reactions invariably lead to cleavage of at least one cobalt-carbon bond, in contrast to the essentially unreactive mono-organocobalt chelates. The increased reactivity observed for the bis-organometallic compounds is presumably a manifestation of the increased electron density on cobalt which activates the organo ligands for electrophilic attack.

Costa and co-workers (42,69) first reported the reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with H_3O^+ . The products CH_4 and $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})]^+$ were identified, but no information regarding the stoichiometry or rate of this reaction was reported. Subsequent titration data indicates that the reaction occurs with the indicated 1:1 stoichiometry (Eqn. 42) (70) and proceeds to completion. Kinetic

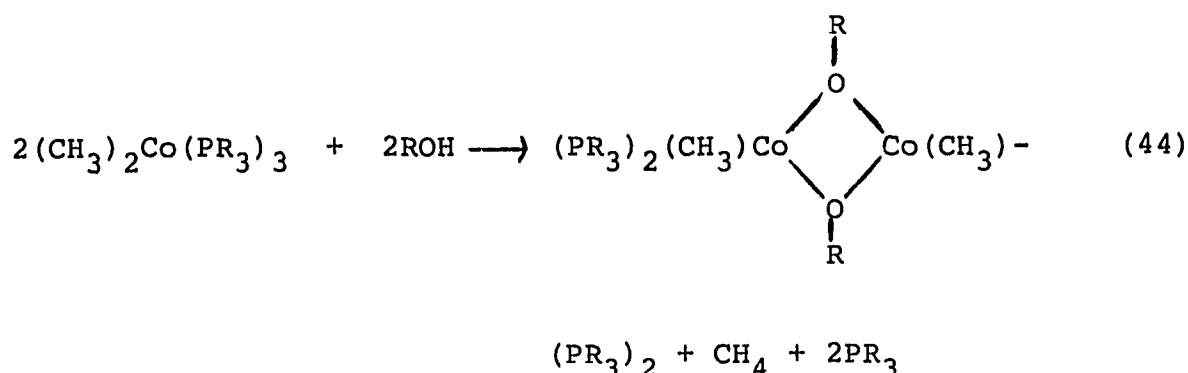


studies by us (70) and Espenson et al. (40) on the reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with excess H_3O^+ show a first-order dependence on the concentration of the dimethyl complex and $[\text{H}_3\text{O}^+]$. The second-order rate constants show a small solvent dependence, and are greater than those determined for $[(\text{CH}_3)_2\text{Co}(\text{tim})]^+$ by a factor of about 15. The slower rate observed for the positively charged $[(\text{CH}_3)_2\text{Co}(\text{tim})]^+$ complex compared to the neutral $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ complex reflects the expected electrostatic repulsion between the two positively charged reactants.

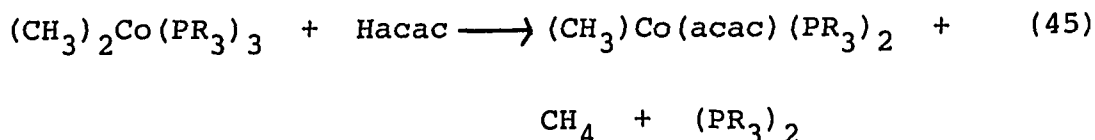
Klein and Karsch (52) reported that weak acids ROH ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) cleave both cobalt-carbon bonds of the divalent complex $(\text{CH}_3)\text{Co}(\text{PR}_3)_3$ with the liberation of two equivalents of methane (Eqn. 43).



These reactions presumably occur in a step-wise fashion since the 1:1 reaction resulted in isolable monomethyl complexes of the composition $[(\text{CH}_3)\text{Co}(\text{PR}_3)_2\text{OR}]_2$ (Eqn. 44).

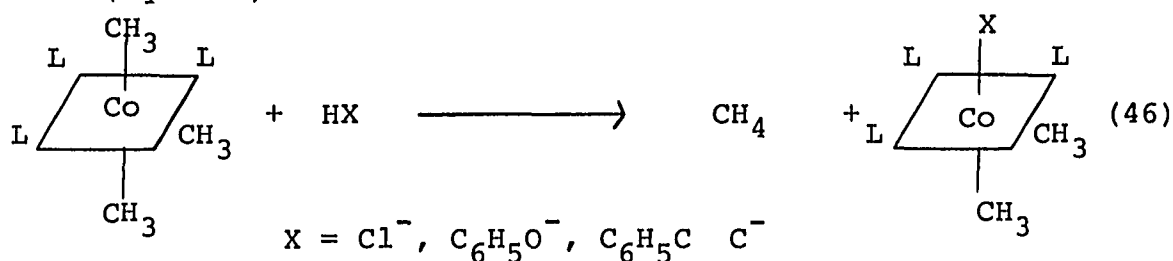


These intermediates are unstable in solutions containing excess ROH however, and decompose further yielding the products shown (Eqn. 43). An exception is the 1:1 reaction of $(\text{CH}_3)_2\text{Co}(\text{PR}_3)_3$ with acacH which gives the more stable $(\text{CH}_3)_2\text{Co}(\text{acac})(\text{PR}_3)_2$ compound (Eqn. 45). The



divalent complex $(C_2H_5)_2Co(bipy)_2$ also reacts with weak acids such as water and alcohol to cleave both Co-C bonds (53).

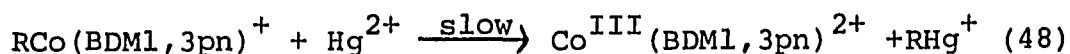
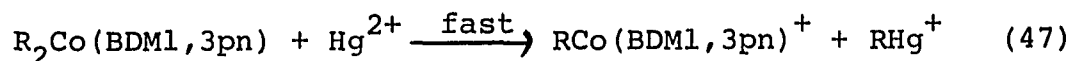
The trimethyl complex $(CH_3)_3Co(PR_3)_3$ reacts with acids to yield from 1 to 3 equivalents of methane (51). Treatment of this complex with a variety of protic acids in the molar ratio acid/complex = 1 results in the elimination of one of the trans methyl groups, and leads to the formation of dimethylcobalt(III) complexes (Eqn. 46).



The remaining methyl groups react further with excess acid to form an additional two equivalents of methane. The enhanced reactivity of trans methyl groups seen in the 1:1 reactions is once again entirely consistent with the well known trans labilizing influence of CH_3 .

Reactions with Metal Electrophiles. In contrast to the mono-organometallic compounds, the reactions of metal electrophiles with bis-organocobalt complexes remain relatively unstudied. Two very recent papers were published however, which described the alkyl and aryl transfer reactions of $R_2Co(BDML,3pn)$, $[R_2Co(tim)]^+$ and $[R_2Co(CR)]^+$ with Hg^{2+} and $C_6H_5Hg^+$. Camus and co-workers (71) studied

the reactions of $R_2Co(BDML,3pn)$ with $HgCl_2$ in acetonitrile ($R = CH_3$). In the presence of excess Hg^{2+} a two step reaction was observed which resulted in the transfer of both methyl groups to mercury (Eqns. 47 and 48). In the



presence of excess complex a third reaction was observed (Eqn. 49) in addition to equation 47. Equation 49 also



occurs with $C_6H_5Hg^+$, and with $(C_6H_5)_2Co(BDML,3pn)$ or $(C_6H_5CH_2)_2Co(BDML,3pn)$ as donors.

Coincidentally, Espenson et al. (40) published the results of a kinetic study on the reactions of $R_2Co(BDML,3pn)$, $[R_2Co(tim)]^+$ and $[R_2Co(CR)]^+$ with $C_6H_5Hg^+$ a short time later ($R = CH_3, C_2H_5, C_6H_5$ etc.). These reactions were very fast in 1:1 THF - H_2O , and in fact when $R = C_6H_5, C_2H_5$ and $n-C_3H_7$ the reactions were too rapid for the stopped-flow technique.

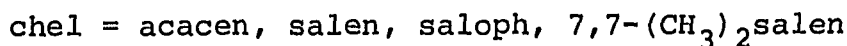
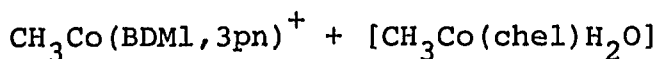
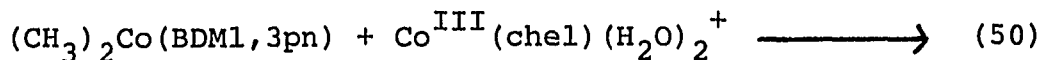
For $R_2Co(BDML,3pn)$, $[R_2Co(tim)]^+$ and $[R_2Co(CR)]^+$ ($R = CH_3$), the reactions with $C_6H_5Hg^+$ follow a second-order rate expression supporting a mechanism in which

there is a direct transfer of a methyl carbanion in a transition state formed by the biomolecular interaction of the dimethyl complex $\text{C}_6\text{H}_5\text{Hg}^+$. The second-order rate constants followed the order $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn}), 2 \times 10^6$; $>[(\text{CH}_3)_2\text{Co}(\text{CR})]^+ (2.1 \pm 0.3) \times 10^5$; $>[(\text{CH}_3)_2\text{Co}(\text{tim})]^+, (1.3 \pm 0.3) \times 10^5$. The slower rates observed for $[(\text{CH}_3)_2\text{Co}(\text{tim})]^+$ and $[(\text{CH}_3)_2\text{Co}(\text{CR})]^+$ relative to $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ is consistent with their positive charge, and therefore lower reactivity toward electrophilic reagents.

Additional examples of reactions of bis-organo-cobalt complexes with metal electrophiles include the reactions of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with Ag^+ to form Ag^0 and C_2H_6 (69,70); and the reactions with Zn^{2+} , Cd^{2+} , and Pb^{2+} (70). These reactions will be discussed in a later section of this manuscript. A very recent example is the reaction of $(\text{CH}_3)_2\text{Co}(\text{acac})(\text{PR}_3)_2$ with Hg^{2+} to form $(\text{CH}_3)_2\text{Hg}$ (55). Unfortunately, no details were given for it is not known whether the complex or Hg^{2+} was in excess. In the latter case the formation of dimethylmercury would be significant since it would represent the first reported example of a methyl transfer reaction from a mono-methyl cobalt complex to CH_3Hg^+ .

Costa and co-workers (69) first reported the methyl transfer reactions shown (Eqn. 50). These reac-

tions are analogous to the methyl-transfer reactions



described above since they also occur by an $\text{S}_{\text{E}}2$ mechanism. Other dialkyl complexes studied in this respect include $[(\text{CH}_3)_2\text{Co}(\text{tim})]^+$ and $[(\text{CH}_3)_2\text{Co}(\text{CR})]^+$ (40). The same second-order rate constants observed for the reactions of these complexes with a given diaquo-cobalt chelate suggests that the rate of methyl transfer is controlled by the rate of $\text{Co-H}_2\text{O}$ substitution in the $\text{Co}(\text{chel})(\text{H}_2\text{O})_2$ complexes.

EXPERIMENTAL

Materials

All reagents were utilized as purchased without further purification except where indicated. The ligand components butanedione monoxime and 1,3-propanediamine were purchased from Eastman Chemical Co.. Methyl iodide was purchased from either J. T. Baker Chemical Co. or Mallinckrodt Chemical Works. Methyl- d_3 iodide was obtained from Stohler Isotope Chemical Co.. Cobalt bromide, sodium borohydride and dimethylcadmium were purchases from Ventron. The metal perchlorates $Zn(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$ and $LiClO_4 \cdot 3H_2O$ were purchased from Smith Chemical Co., Columbus, Ohio. The $LiClO_4 \cdot 3H_2O$ which was found to be contaminated with H_3O^+ , was neutralized with LiOH and recrystallized from H_2O .

The solvents methanol, ethanol, and 2-propanol were purchased from Eastman. The alcohols were dried by the method of Wiberg (72), distilled under nitrogen and stored over 4A molecular sieves.

A sample of analyzed hydrocarbons (C_1-C_4) for use in the GLC experiments was purchased from Scott Research Laboratories. Hypo-Vials, Tuf-Bond serum caps, and Mininert valves were purchased from Pierce Chemical Co.. Gas-Tight syringes were obtained from Hamilton. Rubber serum caps were obtained from Arthur H. Thomas Co.

Infrared Spectra

The infrared spectra in the $200\text{--}600\text{ cm}^{-1}$ region were measured with a Beckman Model 12 high resolution spectrophotometer. Samples were prepared as Nujol mulls and applied to a polyethylene support. Spectra in the $400\text{--}4000\text{ cm}^{-1}$ region were measured either with the above instrument or with a Perkin-Elmer Model 337 Grating Spectrophotometer. The samples were prepared as Nujol or halocarbon mulls on a KBr support. Where necessary the instruments were purged with dry N_2 to remove traces of atmospheric water.

Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra were recorded using a JEOL JNM-MN 100 nuclear magnetic resonance spectrometer. The ligand spectrum (BDML,3pn) was measured using DMSO-d_6 with TMS as an internal standard. The spectra of $(\text{CH}_3)_2(\text{BDML,3pn})$ and $(\text{CD}_3)_2\text{Co}(\text{BDML,3pn})$ were measured in deuterio-chloroform or DMSO-d_6 in the dark using either TMS or the CHCl_3 peak as the internal standard.

Electronic Spectra

Routine spectral analyses of the compounds and reactions were run on a Cary Model 14 Recording Spectro-

photometer. The unit was equipped with a T9 water bath which maintained the cell, and sample compartment temperature constant to $\pm 0.1^\circ\text{C}$. Stock solutions (ca. 10^{-3} - 10^{-4}M) of the complexes in an appropriate solvent were prepared in the dark. An aliquot of this solution was pipetted into one of two matched 1 cm silica cells and diluted with solvent. The spectra were then recorded versus a reference cell containing the solvent in the 650-200 nm region.

The anaerobic spectra were obtained by flushing a cell with prepurified nitrogen using a rubber serum cap which was equipped with inlet and outlet needles. An aliquot of the air-free solution, which was prepared in a Hypo-Vial, was then transferred to the cell using a glass syringe.

Gas Liquid Chromatography (GLC)

A Varian Aerograph Series 1860-1 Chromatograph equipped with a flame ionization detector and a 6' x 1/8" Porapak Q (80-100) mesh column was used to identify the gaseous hydrocarbon products. Table II lists the conditions used for identification of the various hydrocarbons which were sampled using a 50 μl Gas-Tight syringe.

Preparation of BDML₃pn (29)

A solution of butanedione monoxime (30 g, 0.3 moles) and 1,3-propanediamine (11.1 g, 0.15 moles) in

Table II. Conditions for GLC Analysis

<u>Compound</u>	<u>Column Temp. (°C)</u>	<u>Flow Rate (l/min.)</u>	<u>Retention Time (min.)</u>
Methane	115	25	0.5
Ethane	115	25	0.9
Propane	115	25	3.1
2-Propanol	115	25	50.0
Methanol	115	25	5.1
Ethanol	115	25	6.5

500 ml of benzene was boiled under reflux for 7 hours. The water from the reaction was collected as formed in a Dean-Stark trap (4.4 ml collected; theoretical 5.4 ml). The product BDML,3pn separated as a thick brown oil upon cooling and was drawn off using a 1ℓ separatory funnel. Upon standing open to the air for 48 hours white crystals began to form which were subsequently dried in a vacuum desiccator overnight. The yield based on 1,3-propanediamine was 30 grams (83%).

Preparation of $[\text{Ni}(\text{BDML},3\text{pn})]\text{ClO}_4$ (73)

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.76 g, 2mmoles) was dissolved in 5 ml of methanol. To this solution was added BDML,3pn (1.0 g, 4 mmoles) in 5 ml of ethanol. An orange crystalline material instantly formed which was filtered, washed with cold methanol and dried in a vacuum desiccator. The crystals were recrystallized from acetone and the melting point (256°C) compared to the literature value (255°C).

Preparation of $[\text{Co}(\text{BDML},3\text{pn})\text{Br}_2]$

A modification of the method of Costa et al. (74) was used. Crude BDML,3pn was dissolved as the oil in 800 ml of acetone and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (60 g, 0.18 moles) was added neat. A green crystalline material precipitated after slowly bubbling air through the solution overnight.

The product was recrystallized from acetone-water (80:1, v/v) and dried in a vacuum desiccator overnight. The yield estimated from the amount of BDML,3pn added (ca. 0.13 moles) was 30.4 g (51%).

Preparation of $[\text{Co}(\text{BDML},3\text{pn})\text{Cl}_2]$

The same method as that used to prepare $[\text{Co}(\text{BDML},3\text{pn})\text{Br}_2]$ was utilized only $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was employed as the cobalt salt.

Preparation of $[\text{Co}(\text{BDML},3\text{pn})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

This complex was prepared by modifying the method of Costa et al. (24). $[\text{Co}(\text{BDML},3\text{pn})\text{Br}_2]$ (4.7 g, 10 mmoles) was suspended in 100 ml of acetone and the bromide precipitated with either aqueous AgClO_4 or AgNO_3 . The solution was warmed and the resulting precipitate of AgBr digested for 20 minutes. The AgBr was filtered using a Buchner funnel and Celite, and the clear red filtrate tested for complete precipitation with a drop of Ag^+ . A 10-fold excess of NaClO_4 was added and the acetone air evaporated in an evaporating dish. After 48 hours large red-purple crystals were obtained and collected by filtration. The yield based on the dibromide complex was 4.7 g (89%).

Preparation of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$

The complex was prepared by a modification of the method used by Costa et al. (35). $[\text{Co}(\text{BDML},3\text{pn})(\text{H}_2\text{O})_2]-$

$(\text{ClO}_4)_2]$ was used as the starting material instead of $[\text{Co}(\text{BDML},3\text{pn})\text{I}_2]$. In this way, contamination of the product by $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{I}]$ was avoided, and high yields were obtained with regularity.

$[\text{Co}(\text{BDML},3\text{pn})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (5.3 g, 10 mmole) was dissolved in 100 ml of methanol in a 500 ml beaker and 5M sodium hydroxide (2 ml, 10 mmole) added dropwise with stirring followed by a second addition of NaOH (2 ml, 10 mmole). The beaker was covered with a black cloth and a 10-fold excess of methyl iodide (12 ml, 200 mmoles) added. The solution was cooled in an ice bath and aqueous NaBH_4 (1g, 26 mmoles) added dropwise which resulted in a bright orange solution. After a period of 5-10 minutes a vigorous reaction took place resulting in orange platelets of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$. The solution was concentrated by evaporation of the methanol in vacuo with a minimum of heat, and the crystals filtered and washed with cold de-ionized water. The yield based on the diaquo starting complex was 2.6 g (79%).

Preparation of $(\text{CD}_3)_2\text{Co}(\text{BDML},3\text{pn})$

$[\text{Co}(\text{BDML},3\text{pn})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (0.53 g, 1 mmole) was dissolved in 15 ml of methanol and the procedure followed as above with the following modifications: a five-fold excess of methyl- d_3 iodide (98.5% d) (0.60 ml, 10 mmole) was added instead of the usual 10-fold excess of methyl iodide. The yield based on the diaquo-complex was 0.27 g

(81%).

Preparation of $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$

$[\text{Co}(\text{BDML},3\text{pn})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (5.3 g, 10 mmole) was dissolved in 100 ml of methanol and a slight excess of methyl iodide (1 ml, 15 mmole) added. The solution was cooled in an ice bath followed by the addition of aqueous NaBH_4 (0.5 g, 13 mmole) which resulted in an orange colored solution. The solution was concentrated in vacuo, followed by the addition of excess NaClO_4 . After standing in the dark overnight in the refrigerator reddish-orange crystals were observed. The crystals were collected by filtration and dried in a vacuum desiccator. The yield based on the starting cobalt complex was 3.2 g (75%).

Alternatively, $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ was acid hydrolyzed with 1M HClO_4 followed by the addition of NaClO_4 which resulted in crystalline $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$.

Determination of Molar Absorptivities

Molar absorptivities of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ and $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$ in $i\text{-C}_3\text{H}_7\text{OH}$ were determined using the Cary 14. Solutions of the complexes were prepared from analyzed samples (Table III). Typically $5 \times 10^{-5}\text{M}$ solutions were prepared in duplicate in the dark under nitrogen. The solution to be analyzed was placed in one of two matched quartz cells of 1 cm path length.

Table III. Analytical Data for Compounds Prepared

<u>Complex</u>	<u>Calculated%</u>			<u>Found%</u>		
	<u>C</u>	<u>H</u>	<u>N</u>	<u>C</u>	<u>H</u>	<u>N</u>
$(\text{CH}_3)_2\text{Co}(\text{BDM1}, 3\text{pn})$	47.56	7.66	17.06	47.64	7.78	17.14
$(\text{CD}_3)_2\text{Co}(\text{BDM1}, 3\text{pn})$	46.68	7.48	16.75	46.59	7.51	16.78
BDM1, 3pn	55.00	8.33	23.23	55.41	8.67	23.52
$[\text{CH}_3\text{Co}(\text{BDM1}, 3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$	32.15	5.36	12.48	32.40	5.48	12.64
$[\text{Co}(\text{BDM1}, 3\text{pn})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	24.72	4.32	10.46	23.20	4.01	10.07
$[\text{Co}(\text{BDM1}, 3\text{pn})\text{Cl}_2]$	35.80	5.19	15.18	35.40	5.09	14.91
$[\text{Co}(\text{BDM1}, 3\text{pn})\text{Br}_2]$	28.80	4.14	12.20	29.21	4.31	12.35

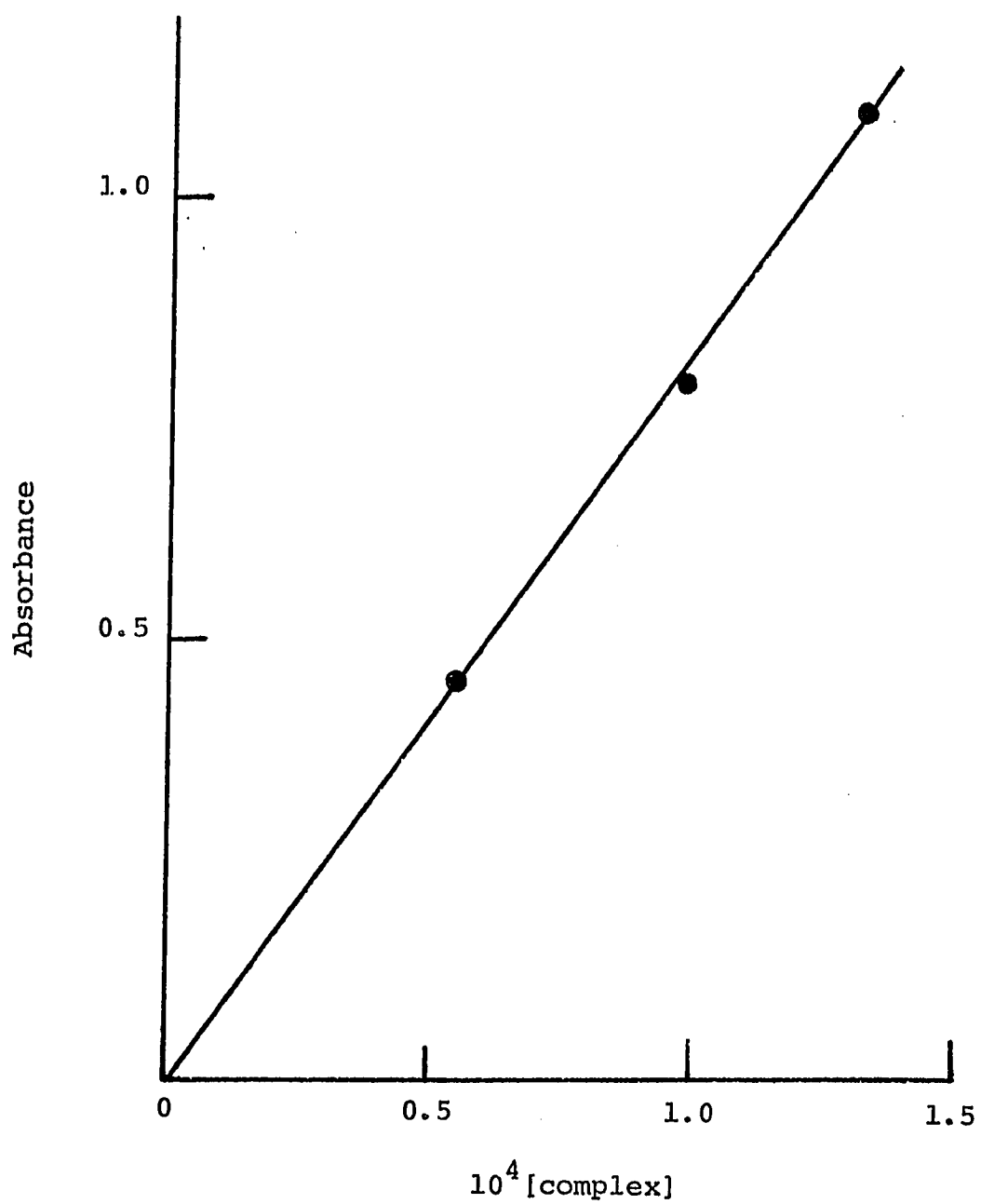


Fig. 6. Beers-Law Plot for the Determination of the Molar Absorptivity Value of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ at 412 nm.

A cell containing $i\text{-C}_3\text{H}_7\text{OH}$ was used as the reference. The spectra were recorded from 650-200 nm, and the molar absorptivity at each absorption band calculated using Beer's-Law. The value at 412 nm for $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ was obtained from the least-squares slope of the Beer's-Law plot shown in Figure 6. The molar absorptivity values are found in Table V in the RESULTS AND DISCUSSION section.

Stability of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in Solution

Stock solutions ($5 \times 10^{-5}\text{M}$) of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in the appropriate solvent were prepared in the dark. Solutions in tetrahydrofuran, acetone, 2-propanol, absolute ethanol, 95% ethanol, methanol, and water were prepared. The reactions were followed as a function of time by observing the disappearance of the visible maximum at 412 nm due to $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$; or the appearance of the band at 460 nm due to $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})]^+$.

Solution Photolysis of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$

Identification of Products

Stock solutions ($1 \times 10^{-4}\text{M}$) of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in anhydrous methanol, ethanol and 2-propanol were prepared in the dark and transferred to 6 ml Hypo-Vials. The vials were sealed with Tuf-Bond serum caps and the solutions either deoxygenated with N_2 or oxygenated with air.

The solutions were irradiated with the unfiltered light of a 150 W Sylvania spot light set 10 inches from the vials. A stream of cold air was passed over the vials to keep the solutions cool. The temperature during photolysis never exceeded 27°C. The alkane products were identified by GLC, and the complex products identified by comparing the electronic spectra of the photolyzed solutions to the solution spectra of known complexes which were prepared as follows.

$[\text{Co(II)(BDM1,3pn)}]^+$. $[\text{CH}_3\text{Co(BDM1,3pn)H}_2\text{O}]\text{ClO}_4$ was photolyzed under anaerobic conditions in the appropriate solvent. The spectrum of the resultant red solution was recorded.

$[\text{Co(I)(BDM1,3pn)}]$. $[\text{Co(III)(BDM1,3pn)(H}_2\text{O)}_2]-(\text{ClO}_4)_2$ in basic methanol, ethanol, or 2-propanol was reduced to the royal blue Co(I) complex using NaBH_4 . Addition of CH_3I resulted in $[\text{CH}_3\text{Co(III)(BDM1,3pn)}]^+$ thus proving the existence of Co(I).

$[\text{CH}_3\text{Co(I)(BDM1,3pn)}]^-$. $[\text{CH}_3\text{Co(III)(BDM1,3pn)H}_2\text{O}]$ was reduced with NaBH_4 as above resulting in a green colored solution. Addition of CH_3I resulted in $(\text{CH}_3)_2\text{Co-(BDM1,3pn)}$ as expected.

Kinetics of Photolysis of $(\text{CH}_3)_2\text{Co(BDM1,3pn)}$

Solutions (ca. $1 \times 10^{-4}\text{M}$) of $(\text{CH}_3)_2\text{Co(BDM1,3pn)}$ in anhydrous methanol, ethanol and 2-propanol were prepared in the dark. The reactions were effected in quartz

cells (1-cm path) as described above. Typically, one cell was deoxygenated with N_2 and the other oxygenated with breathing air for 5 minutes in the dark. The reaction was initiated by turning on the light source for the desired period of time. The reactions were quenched after each interval by covering the cells with a black cloth and placing them in the sample compartment of the Cary 14. The change in concentration of $(CH_3)_2Co(BDM1,3pn)$ was measured by the change in absorbance at 412 nm ($\epsilon = 8380$). Only the anaerobic reactions followed the first-order rate law, and these data are tabulated in APPENDIX II.

Mass Spectral Analysis of Hydrocarbons

$(CD_3)_2Co(BDM1,3pn)$ or $(CH_3)_2Co(BDM1,3pn)$ (0.033 g, 0.1 mmole) was dissolved in the dark in 25 ml of dry 2-propanol in a specially designed 50 ml round bottom flask. The flask was constructed such that a high vacuum stopcock connected the flask to a female ground glass joint. The flask was fitted with a rubber serum-cap and flushed with N_2 for 15 minutes to a final pressure of 1 atmosphere. The solution was photolyzed for the desired number of hours by two 150 W Sylvania spot lights. The flask was cooled in an ice bath and the solution stirred with a magnetic stirrer to prevent localized heating. The solutions generally turned blue-green in a matter of minutes.

Table IV. Mass Spectral Data^a for the Photolysis of $(CD_3)_2Co(BDML,3pn)$.

<u>75eV</u>			<u>10eV</u>		
<u>Ion</u>	<u>m/e</u>	<u>Relative Intensity</u>	<u>Ion</u>	<u>m/e</u>	<u>Relative Intensity</u>
H	1	2.1		-	
H ₂ , D	2	1.9		-	
HD	3	0.1		-	
D ₂	4	0.9		-	
C	12	2.3		-	
CH	13	1.5		-	
N, CD	14	off scale		-	
CHD	15	6.7		-	
CD ₂	16	13.2		-	
CHD ₂	17	51.1	CHD ₂	17	1.5
H ₂ O, CD ₃	18	27.7	H ₂ O	18	3.0
CHD ₃	19	100	CHD ₃	19	100

^aSolutions of $(CD_3)_2Co(BDML,3pn)$ in 2-propanol photolyzed at room temperature then cooled to -78°C.

The flask containing the photolyzed samples described above was connected to the inlet system of a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer via the ground glass joint. The flask was subsequently cooled to a temperature of -78° with a dry-ice acetone bath, and the spectrum recorded. Standard samples of CD_3H (M/e 19) and CH_4 (M/e 16) were used in order to establish the optimum conditions for the analysis. The electron energy which was most suitable was found empirically by repeatedly scanning the mass region of interest while stepwise decreasing the potential from 75 ev. The potential (10 ev) at which the parent ion peak was sufficiently intense for accurate measurement, and at which peaks due to fragmentation had disappeared, was chosen. The sensitivity and slit width was varied depending upon the peak height and resolution desired. A background spectrum was obtained with pure 2-propanal under identical conditions.

Reaction with H_3O^+

The stoichiometry of the reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with H_3O^+ was determined by spectral titration of ca. 10^{-4}M solutions of the dimethyl complex with a standard solution of HClO_4 in 2-propanol. The absorbance decrease at 412 nm due to $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ was followed after each addition of the HClO_4 titrant from a 1 μl syringe. The complex products were identified spectro-

photometrically and the gaseous hydrocarbon (CH_4) by GLC analysis.

The following procedure was used to prepare the HClO_4 solution. Concentrated (70%) HClO_4 was standardized against a 0.5000 M NaOH solution by titration. Exactly 10.0 ml of the 11.45 M HClO_4 solution was pipetted into a 100 ml volumetric flask and the solution diluted to the mark with 2-propanol. The final concentration was 1.145 M.

Kinetic determinations were carried out spectrophotometrically utilizing the Cary 14. The rates were determined by monitoring the decrease in absorbance of the dimethyl complex at 412 nm as a function of time. Pseudo-first order conditions were employed by utilizing 10^{-4} M solutions of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ and 1.145×10^{-3} - 2.86×10^{-3} M solutions of H_3O^+ . The ionic strength of the solutions was maintained at 0.05 or 0.10M using $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. The reactions were initiated by adding the H_3O^+ solution from a 10 μl syringe. In each case the reaction chamber was thermostated at $25.0 \pm 0.2^\circ\text{C}$. The data (APPENDIX III) were analyzed using a least-squares computer program (STATPACK).

Reactions of $[(CH_3)_2Co(BDML,3pn)]$ with Metal Ions

Several metal ions were screened for their ability to react with $(CH_3)_2Co(BDML,3pn)$. Generally, solutions of the metal perchlorates in either methanol or 2-propanol were added in excess to solutions of the complex under N_2 . The absorption at 412 nm was monitored in the usual manner.

Of the ions tested $HgCl_2$, Ag^+ , Cu^{2+} , Cr^{3+} , Cd^{2+} , Zn^{2+} , and Pb^{2+} reacted. The reactions were always instantaneous. Solutions of $Ni(ClO_4)_2 \cdot 6H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$ reacted only very slowly, and this reaction could not be distinguished from the reaction of $(CH_3)_2Co(BDML,3pn)$ with the solvent. It appears that Co^{2+} reacts very fast in the presence of O_2 , however (75).

Reactions with Ag^+

To a solution of $(CH_3)_2Co(BDML,3pn)$ in a methanol at $-78^\circ C$ was added an excess of methanolic $AgNO_3$ solution at $-78^\circ C$. A yellow-brown precipitate slowly formed which was stable at this temperature. Gradual warming to an $-50^\circ C$ by standing at room temperature resulted in a vigorous gas evolution, and a silver metal precipitate. The gas was primarily C_2H_6 with some CH_4 . The precipitate was separated from the solution by quickly centrifuging the cold mixture. Upon warming the isolated material a vigorous gas evolution was again observed with the

simultaneous formation of Ag° . The gaseous products were mostly C_2H_6 .

The reaction was run in several solvents at room temperature to determine the solvent dependence of the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio. $(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$ (0.001 g, 3×10^{-6} moles) was dissolved in 15 ml of H_2O^* , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$ in 50 ml Hypo-Vials which were fitted with serum caps, and flushed with N_2 for 10 minutes. The flasks were covered with aluminum foil to keep out light, and AgNO_3 (0.5 ml of a 1M aqueous solution) was injected to initiate the reaction. A black precipitate of silver immediately formed in all cases. The $\text{CH}_4/\text{C}_2\text{H}_6$ ratio was calculated by disc integration of the GLC peaks.

Preparation of Stock Metal Solutions

Solutions of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Pb}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were prepared in $i\text{-C}_3\text{H}_7\text{OH}$. The final concentrations were approximately 0.25M, 0.25M and 0.1M respectively. The Zn^{2+} and Pb^{2+} solutions were standardized by complexometric titration using EDTA as the primary standard (76).

All glassware was cleaned by soaking in 6M HNO_3 and rinsed with distilled-deionized water. Analytical

*1 ml of CH_3OH was used to dissolve the complex.

grade (ethylenedinitrilo)-tetraacetic acid disodium salt was dried at 120°C for 8 hours. The EDTA (28.6460g, 0.0770 moles) was weighed into a 500 ml volumetric flask, dissolved, and diluted to the mark with H₂O. The solution was then transferred to an acid washed polyethylene bottle for storage. The final concentration was 0.1539M.

A NH₄Cl-NH₃ buffer (pH 10) was prepared by dissolving NH₄Cl (7.0 g, 0.14 moles) in concentrated NH₄OH (60 ml) and diluting to the mark in a 100 ml volumetric flask with H₂O.

The Pb²⁺ solution (25.00 ml) was pipetted into a 250 ml erlynmeyer flask and diluted with 40 ml of H₂O. A spatula tip of tartaric acid was added as an auxiliary complexing agent followed by 5 ml of the pH 10 buffer. Solid Erichrome Black-T indicator was added and the solution titrated to a blue end point with the EDTA solution. The procedure was repeated two more times to yield a mean Pb²⁺ concentration of 0.1010 M.

The Zn²⁺ solution was titrated in a similar fashion only tartaric acid was not added. The final concentration was 0.2499 M.

The Cd(ClO₄)₂·6H₂O solution was standardized by atomic absorption spectrophotometry. A standard curve was prepared using solutions prepared from a 1000 ppm Cd²⁺ solution in 0.1M HNO₃. The final concentration was 0.2485 M.

Spectral Titrations with Zn^{2+} , Cd^{2+} , and Pb^{2+}

The titrations were carried out anaerobically in a 1 cm quartz cell using a Cary Model 14 recording spectrophotometer. Typically 10^{-4} M solutions of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ were titrated with standard solutions of the metal salts by following the absorbance decrease due to $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ at 412 nm. The fast first reaction' of the overall biphasic reaction was titrated by injecting small volumes of the M^{2+} titrant from a 1 μl syringe directly into the cell containing the appropriate volume of complex. Mixing times were on the order of 5 sec using this procedure. By repeating this process as rapidly as possible, the titration could be completed in a few minutes, thereby minimizing any error due to the second slower reaction. The overall reaction was titrated by simply allowing the reaction to proceed to completion following the addition of M^{2+} .

Kinetics of Methane Evolution

Typically $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ (0.03g, 0.1 mmol) was dissolved in 100 ml of $i\text{-C}_3\text{H}_7\text{OH}$ in a specially designed apparatus in which the reaction vessel and serum cap were separated by a stopcock. Alternatively a 125 ml Hypo-Vial and Mini-nert valve were used. The Tuf-Bond serum caps were found to leak after puncture and were

not used. The rubber serum caps were found to be satisfactory, however, if relatively few punctures were made. The reactions were initiated using standardized metal ion solutions. The liberated methane was sampled in 20 μ l aliquots as a function of time using 50 μ l Hamilton Co. Gas-Tight syringe, and detected by GLC using a Varian Aerograph Series 1860-1 Chromatograph equipped with a flame ionization detector and a 6' x 1/8" Porapak Q (80-100) mesh column maintained at 110°C. The infinity value was determined by acid hydrolysis of the reaction mixture, or allowing the reaction to proceed to completion.

Effect of CH_3OH and H_2O on the

Rate of Methane Evolution

$(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$ (0.033g, 0.1 mmole) was dissolved in 80 ml of 2-propanol in a Hypo-Vial and the solution deoxygenated with N_2 . Deoxygenated CH_3OH or H_2O (20 ml) was added by syringe and the reaction initiated with the appropriate metal ion solutions (1 mmole). The rate of methane evolution was monitored as before. For all three metal ions the theoretical amount of methane was evolved in ca. 1 hour. The reaction with Cd^{2+} was carried out in pure methanol as above and the theoretical amount of methane was evolved in less than one hour.

Simultaneous Titration and Methane Evolution
for the Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with Cd^{2+}

$(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ (0.0339g, 1×10^{-4} moles) was dissolved in 100 ml of 2-propanol in a 125 ml Hypo-Vial. The vial was sealed with a rubber serum cap and the solution deoxygenated with N_2 . The complex was titrated with a 0.25M $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ solution in 50 μl increments. The reaction was allowed to proceed for ca. 30 minutes in order to ensure completion of the second step of the overall biphasic reaction.

The amount of methane liberated after each addition was monitored by GLC and compared to the theoretical value as determined by acid hydrolysis of an equivalent quantity of the complex. Subsequently a 0.3 ml aliquot of the solution was transferred from the vial to air free 1 cm quartz cell which contained 2.7 ml of deoxygenated 2-propanol. The absorbance at 412 nm was recorded and the procedure repeated.

Reaction of $(\text{CH}_3)_2\text{Cd}$ in 2-propanol

Nitrogen was bubbled through 100 ml of dry 2-propanol in a 125 ml Hypo-Vial which was sealed with a rubber serum cap. The vial was covered with aluminum foil and $(\text{CH}_3)_2\text{Cd}$ (14.5 μl , 10^{-4} moles) added using a 50 μl syringe which had been purged with N_2 . The methane evolved

was followed as a function of time by GLC. An instantaneous reaction liberated one equivalent of methane. This reaction was followed by a slow reaction during which an additional equivalent of methane was evolved.

Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with CdCl_2
in Methanol

A $5 \times 10^{-3}\text{M}$ solution of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in dry methanol was prepared in a 50 ml Hypo-Vial. The vial was sealed with a rubber serum cap and the flask deoxygenated with N_2 in the dark. An excess of a methanolic solution of CdCl_2 was added using a syringe to initiate the reaction. Methane was evolved, and after several minutes a white precipitate formed. The solid was collected by centrifuging the solution, and washed with cold methanol until the wash solution was colorless. A portion of the solid was taken for qualitative analysis of Cd^{2+} and Cl^- (77). The remainder was dried in a vacuum desiccator and used for IR analysis. The positive tests for Cd^{2+} and Cl^- , the presence of C-H stretching bands at 2960 and 2830 cm^{-1} , and the strong absorption at 995 cm^{-1} suggests the compound is $\text{CdCl}(\text{OCH}_3)$.

Kinetics for the Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$
with Excess Metal Ion

The time dependence of these reactions was followed in a Durrum-Gibson stopped-flow single beam spectro-

photometer, with a Kel-F flow path and a 2 cm path length cuvette. All reactions were temperature controlled with a precision of $\pm 0.1^\circ\text{C}$ by means of submersion of the drive syringes, the Kel-F path and reaction cuvette in a water reservoir. The water reservoir was connected in continuous flow with a thermostated P.M. Tamson (N.V.) bath. The kinetics were studied at 22.2°C in freshly distilled $i\text{-C}_3\text{H}_7\text{OH}$ using ca. 7.5×10^{-6} M solutions of $(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$ and an excess of metal ion. The ionic strength was maintained at 1.8×10^{-3} M using lithium perchlorate.

The pseudo-first order kinetic traces were recorded on a Tektronix storage oscilloscope as a trace of voltage versus time. A permanent record of the reactions was obtained by photographing each trace with a Tektronix Oscilloscope Camera C-27 using a Polaroid Film Pack Type 107. The photographs were xeroxed and the traces smoothed by hand using a French Curve. The tedious procedure of digitalizing the data was performed manually with a Picket No. 33E rule which was calibrated in 0.01 inches. The deflection at any given time was taken to be the distance from the voltage output (%Trans) at infinite time, to the trace. These measurements were used to compute the k_{obs} values using the computer program TRDATA*.

*T. S. Shoupe, Ph.D. Dissertation, University of New Hampshire (1976).

The $k_{\text{obs}}/[M^{2+}]$ values summarized in Table XI represent the mean values of at least five independent determinations for each concentration of metal ion. Standard deviations were on the order of 5-10% for both the Zn^{2+} and Cd^{2+} reactions. The solutions were thoroughly deoxygenated with nitrogen prior to running the reactions; however, the solutions used in the stopped-flow experiments could not be kept entirely air free.

Preparation of $\text{ClCH}_2\text{OCH}_3$ (78)

Sodium metal (5.75g, 0.25 g-atoms) was dissolved in 200 ml of CH_3OH in a 3-neck round bottom flask. The flask was attached to a 2 foot fractionating column which had a side-arm and cold trap at the top. The solution was cooled to 0°C in an ice bath and the reaction initiated with ethyl iodide (40g, 0.25 moles). The solution was stirred for 1 hour and then warmed slowly to room temperature. The ether passed through the column as a gas and was trapped at -78°C . The ether was analyzed by GLC and found to be pure.

Attempt to Trap CH_3Cd^+ with $\text{ClCH}_2\text{OCH}_3$

$(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$ (0.16g, 0.5 moles) was dissolved in 100 ml of 2-propanol in a 3-neck round bottom flask, and the solution deoxygenated with N_2 . $\text{Cd}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ (2 ml, 0.5 mmoles) of a 0.25M solution in 2-propanol was

added using a syringe. The reaction mixture was subsequently cooled in an ice bath and $\text{ClCH}_2\text{OCH}_3$ (0.4 ml, 5 mmoles) added. After allowing 1 hour for the reaction to occur the solution was distilled into a trap which was cooled to -78°C to prevent possible loss of the methyl ethyl ether (b.p. 8°C). The distillate was analyzed for $\text{CH}_3\text{CH}_2\text{OCH}_3$ by GLC without success.

Preparation of $[\text{CH}_3\text{Cd}(\text{i-OC}_3\text{H}_7)]_4$ (79)

The following synthesis was carried out in a glove bag under an atmosphere of N_2 . A solution of air-free anhydrous 2-propanol (1.2g, 0.02 moles) in hexane (10 ml) was slowly added via syringe to a solution of $(\text{CH}_3)_2\text{Cd}$ (2.8g, 0.02 moles) in hexane (40 ml). The reaction was carried out at -78°C in a 125 ml Hypo-Vial. Upon warming the solution to room temperature methane was evolved and a colorless solid formed. The mixture was warmed to 40°C to dissolve the solid. Upon cooling in an ice bath the isopropoxide crystallized as colorless needles.

Isolation of $[\text{CH}_3\text{Cd}(\text{i-OC}_3\text{H}_7)]_4$ from the
Reaction of the Dimethyl Complex with
 Cd^{2+} ($[\text{Cd}^{2+}]/[\text{complex}] = 0.5$).

$(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ (0.33g, 1×10^{-3} moles) was ground in an agate mortar and pestle and dissolved in

200 ml of 2-propanol in a two-neck round bottom flask. The flask was sealed with a stopcock, and with a Schlenk tube. A piece of glass wool was placed inside the Schlenk tube in order to filter any insoluble matter during the extraction procedure. The solution was flushed with N_2 followed by several evacuation and N_2 purge cycles. The reaction was initiated with a deoxygenated anhydrous 0.25M Cd^{2+} solution (2.0 ml, 5×10^{-4} moles) in 2-propanol. An instantaneous color change from orange to red-orange was observed. The reaction was allowed to proceed for approximately one hour at $0^\circ C$. The solvent was removed by freeze drying and the residue extracted with 30 ml of deoxygenated hexane. The extract was filtered through the glass wool and collected in the Schlenk tube. The volume of hexane was reduced in vacuo and the solution transferred to a sublimation apparatus inside a glove bag. The residue was sublimed at 10^{-3} Torr (determined by a McLeod gauge) at approximately $115^\circ C$. A small amount of white material was recovered which was soluble in hexane, and which decomposed in H_3O^+ with the liberation of methane. The solid material was analyzed by mass spectral analysis.

Isolation of the Lead Containing
Precipitate from the Reaction of
 $(CH_3)_2Co(BDM1,3pn)$ with Pb^{2+} .

$(CH_3)_2Co(BDM1,3pn)$ (0.164g, 5×10^{-4} moles) was

ground in an agate mortar and pestle and dissolved in 100 ml of 2-propanol in a 125 ml Hypo-Vial. The vial was sealed with a rubber serum cap and the solution flushed with N_2 to remove O_2 . A 0.1M solution of Pb^{2+} in 2-propanol was deoxygenated with presaturated N_2 and 2.5 ml (2.5×10^{-4} moles) added using a syringe. The orange colored solution of the dimethyl complex instantly became red-orange in color. After approximately 5 minutes a dark-brown precipitate began to form. The solution was cooled overnight in a refrigerator to allow the solid material to settle. The Hypo-Vial was opened in an atmosphere of N_2 using a glove bag, and the supernatant liquid transferred via micropipet to several test tubes. After capping the test tubes with rubber serum caps the solutions were centrifuged and the recovered precipitates washed with cold 2-propanol until the wash solution was colorless. The precipitates were dried in vacuo and analyzed by elemental analysis, UV-Vis and GLC.

RESULTS AND DISCUSSION

Synthesis and Characterization of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$

Synthesis

The most generally useful and convenient method for the synthesis of symmetric dialkylcobalt(III) complexes containing a stabilizing macrocyclic ligand system is via the reaction of the corresponding monoalkylcobalt(I), $\text{RCo}^{\text{I}}(\text{chel})$ complex with alkyl halides. These Co(I) intermediates can be generated either in situ or in some cases isolated in an oxygen-free atmosphere. Although the latter method was employed successfully in the preparation of $[\text{R}_2\text{Co}(\text{tim})]^+$ and $[\text{R}_2\text{Co}(\text{CR})]^+$ (36), a polarographic study by Costa et al. (39) indicated that $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})]^-$ was unstable even in aprotic solvents. As a consequence, $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})]^-$ probably is not isolable, and the in situ method was selected as the best route to $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$.

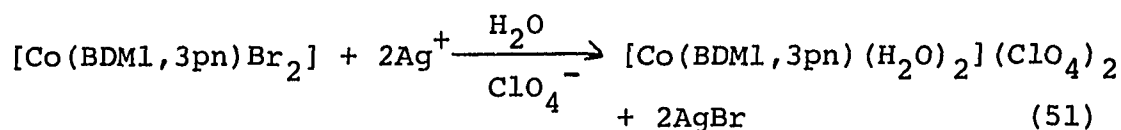
Initially certain difficulties were experienced in the preparation of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$. First, the preparation of the macrocyclic ligand BDML,3pn by the condensation of two moles of 2,3-butanedionemonoxime and 1,3-propanediamine in benzene resulted in the formation of a viscous brown oil which was not easily crystallized.

Early attempts to solidify the oil by stripping off the excess benzene in vacuo, or drying the oil in a vacuum desiccator all failed. Eventually, crystalline BDML,3pn was prepared by simply allowing the oil to air-dry for a period of 48 hours. Although the literature melting point value was never reproduced, elemental analysis, and the preparation of the nickel perchlorate derivative $(\text{Ni}(\text{BDML},3\text{pn})]\text{ClO}_4$ confirmed that the ligand had been synthesized.

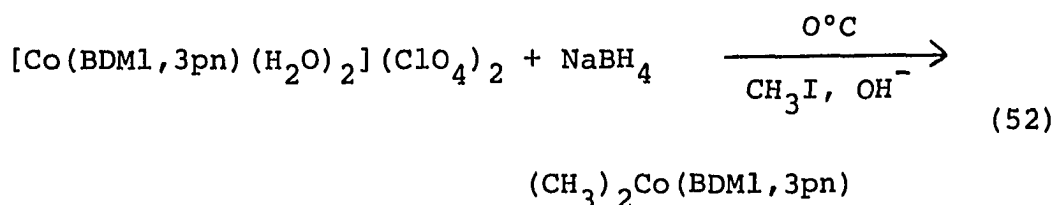
Secondly, all attempts to prepare $(\text{CH}_3)_2\text{Co}-(\text{BDML},3\text{pn})$ by the method of Schrauzer (31) or by the sodium borohydride reduction of $[\text{Co}^{\text{III}}(\text{BDML},3\text{pn})\text{X}_2]$ ($\text{X} = \text{Cl}^-$ or Br^-) in the presence of methyl iodide, either failed completely or resulted in very low yields. Thus, when $[\text{Co}(\text{BDML},3\text{pn})\text{Br}_2]$ was reacted with an excess of NaBH_4 in basic methanol a very rapid color change to the deep-blue color of $[\text{Co}^{\text{I}}(\text{BDML},3\text{pn})]$ was observed. However, upon addition of CH_3I or dimethyl sulfate only the formation of $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})]^+$ was observed spectrophotometrically. By reducing $[\text{Co}(\text{BDML},3\text{pn})\text{Br}_2]$ in the presence of CH_3I both $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ and $[\text{CH}_3\text{Co}-(\text{BDML},3\text{pn})]^+$ were formed, and small yields of the dimethyl derivative were isolated. The failure to isolate $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in high yields in these reactions was presumably due to the strong coordinating strength of Br^- .

Slightly better yields (26% based on Co) were obtained by reducing a mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, BDML,3pn , and CH_3I with carbon monoxide in 50% aqueous-THF. This route was a modification of the method used by Costa et al. (35) to prepare other dialkyl and mixed alkyl-aryl cobalt complexes of BDML,3pn . Although the yields of $(\text{CH}_3)_2\text{Co}(\text{BDML,3pn})$ obtained in the carbon monoxide preparation were acceptable for routine use, a better method of synthesis was needed for the preparation of the deuterium labeled complex $(\text{CD}_3)_2\text{Co}(\text{BDML,3pn})$.

Several syntheses were tried using a variety of alkylating agents, cobalt complexes, reducing agents, and solvents. The sodium borohydride reduction of the diaquo-complex $[(\text{Co}(\text{BDML,3pn})(\text{H}_2\text{O})_2)(\text{ClO}_4)_2]$ in the presence of excess methyl iodide resulted in the highest yields. The diaquo-complex was prepared in crystalline form by precipitating the bromide of $[\text{Co}(\text{BDML,3pn})\text{Br}_2]$ with AgClO_4 or AgNO_3 , followed by the addition of excess ClO_4^- in aqueous-acetone (Eqn. 51). Subsequent reduction of the



diaquo-complex with NaBH_4 in basic aqueous-methanol, in the presence of an excess of CH_3I resulted in high yields of the dimethyl complex (Eqn. 52). By using methyl iodide



- d_3 as the alkylating agent the labeled complex $(\text{CD}_3)_2\text{Co}(\text{BDMl},3\text{pn})$ was prepared.

An unusual feature of this synthesis was the induction period which occurred subsequent to the addition of NaBH_4 . This ten minute period was invariably followed by a very vigorous reaction which resulted in the formation of crystalline $(\text{CH}_3)_2\text{Co}(\text{BDMl},3\text{pn})$. For example, when running the reaction on a 10 mmole scale in 100 ml of methanol, a 1 liter beaker was required in order to contain the reaction. Although a number of approaches were tried in an effort to control this reaction it was not possible. Low temperatures served only to prolong the induction period. Sodium borohydride was added neat in both pellet and powder form to no avail. The dropwise addition of an aqueous solution of NaBH_4 also resulted in the same vigorous reaction. One explanation might be that the crystallization of $(\text{CH}_3)_2\text{Co}(\text{BDMl},3\text{pn})$ initiates this reaction since no crystals were observed up to this point, even though spectrophotometric measurements indicate that the complex was formed in solution.

Characterization

The $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ and $(\text{CD}_3)_2\text{Co}(\text{BDML},3\text{pn})$ complexes were characterized by their electronic, ^1H -NMR, and IR spectra. The results of elemental analyses (Table II) clearly reveal the purity of these complexes. They are both light sensitive in solution, particularly in the presence of oxygen, however they are relatively stable in the solid state. These reactions will be the subject of a future section.

Electronic Absorption Spectra. The electronic spectrum (650–220 nm) of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ was recorded in a variety of solvents including CH_3OH , THF and $i\text{-C}_3\text{H}_7\text{OH}$, and the molar absorptivity values were determined for all of the bands in $i\text{-C}_3\text{H}_7\text{OH}$. In addition, the spectrum and molar absorptivities of $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{H}_2\text{O}]\text{-ClO}_4$ were determined in $i\text{-C}_3\text{H}_7\text{OH}$ (Table V).

The spectrum of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ was identical in all three solvents and consists of two well resolved bands at 410 and 238 nm, and a poorly resolved shoulder at ca. 280 nm (Fig. 7). The position of the low energy band is in qualitative agreement with the value reported by Schrauzer et al. (31) (408 nm) for the same complex in CH_3OH . However their reported molar absorptivity value ($\epsilon = 6700$) is considerably lower than that found here ($\epsilon = 8380$). Presumably, the low ϵ value reported

Table V. Electronic Absorption Spectra of Complexes Prepared

<u>Complex</u>	<u>Wavelength (nm)^a</u>			
$[\text{CH}_3\text{Co}(\text{BDM1}, 3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$	463 (2113)	398 (1530)	325 (4295) sh	275 (10,080)
$(\text{CH}_3)_2\text{Co}(\text{BDM1}, 3\text{pn})$	410 (8380)	-	280 (11,520) sh	238 (20,900)
$[\text{Co}^{\text{III}}(\text{BDM1}, 3\text{pn})\text{Br}_2]$	-	-	300	233
$[\text{Co}^{\text{III}}(\text{BDM1}, 3\text{pn})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	-	-	300	240
$[\text{Co}^{\text{I}}(\text{BDM1}, 3\text{pn})]$	665	-	-	-
$[\text{CH}_3\text{Co}^{\text{I}}(\text{BDM1}, 3\text{pn})]^-$	640	-	-	-
$[\text{Co}^{\text{II}}(\text{BDM1}, 3\text{pn})]^+$	519	-	-	-

^aMolar absorptivities ($\text{cm}^{-1} \text{M}^{-1}$) in parenthesis

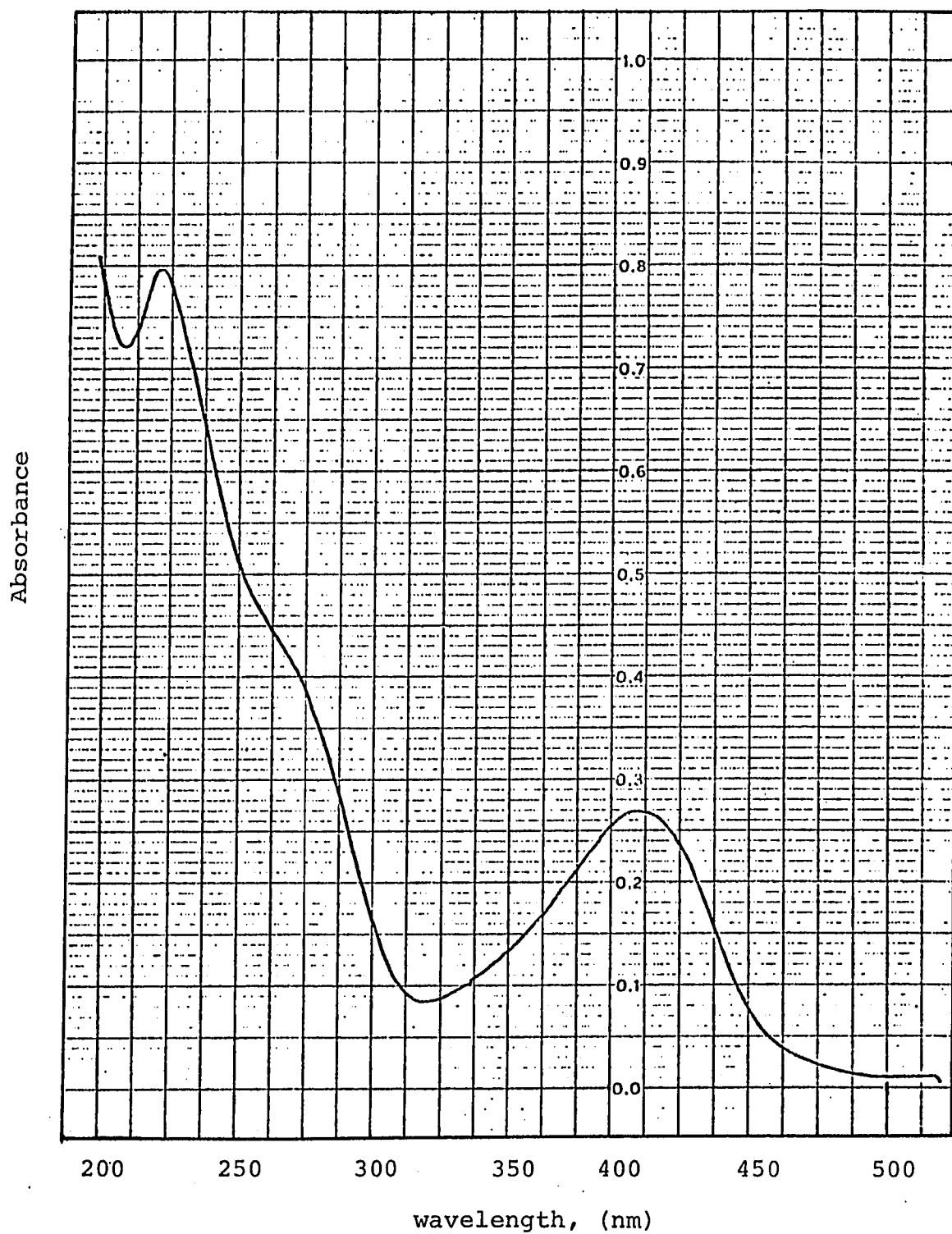


Fig. 7. Electronic Spectrum of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in 2-propanol.

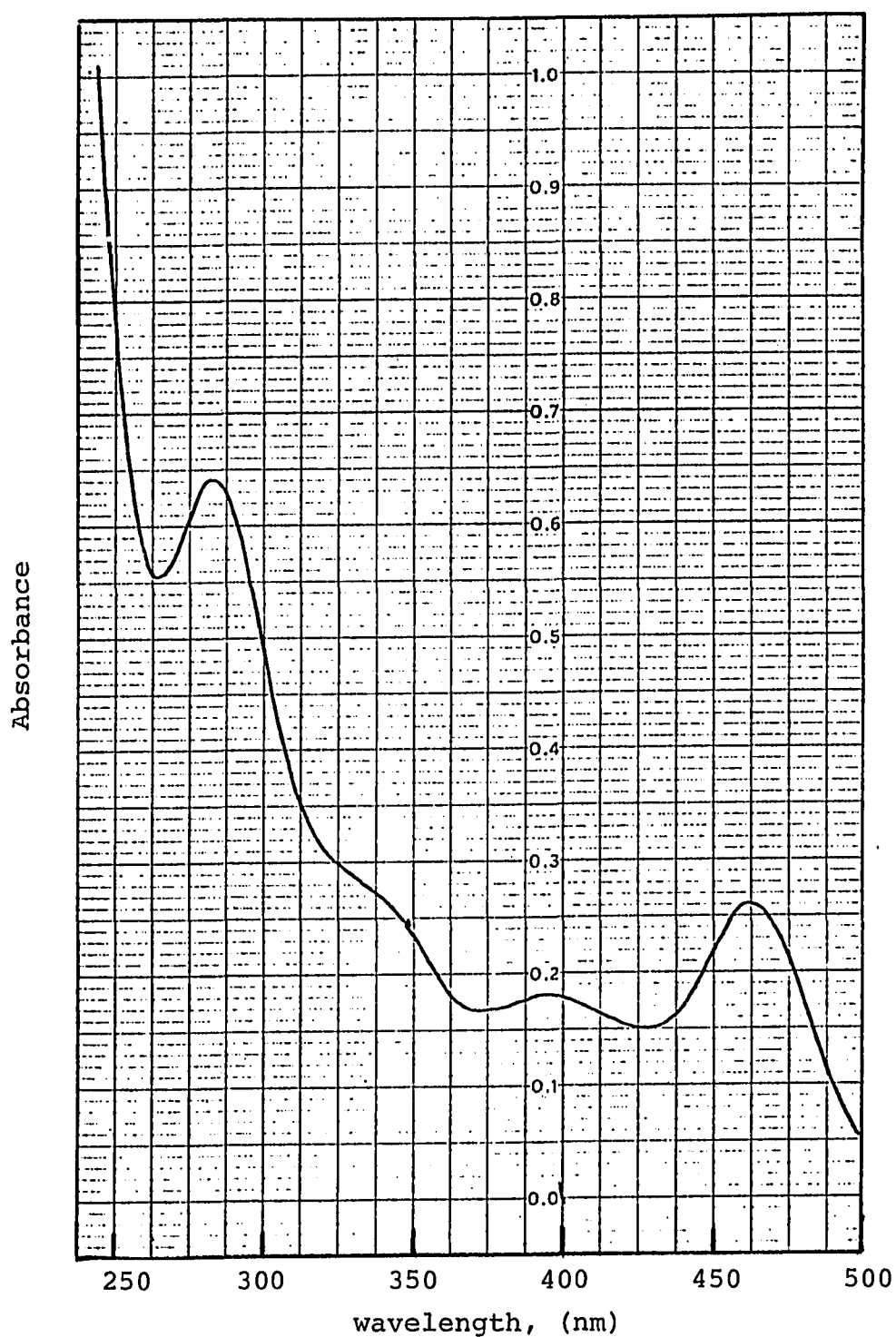
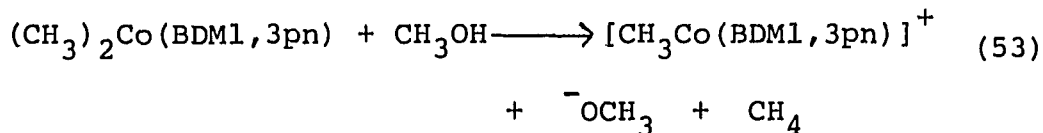


Fig. 8. Electronic Spectrum of $[\text{CH}_3\text{Co}(\text{BDM1,3pn})\text{H}_2\text{O}]\text{ClO}_4$ in 2-propanol.

by these authors resulted from a loss of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ due to its reaction with CH_3OH (Eqn. 53). Similar diffi-



culties were encountered in this work, and no attempt was made to determine the molar absorptivities of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in this solvent.

The electronic spectra of other dialkyl cobalt complexes have not been reported in the literature, consequently no attempt will be made to assign the bands observed for $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$. However, it is interesting to compare the spectrum of the dimethyl complex to that of the corresponding monomethyl complex $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$.

The electronic spectra of monoalkyl cobalt complexes containing oxime and imine macrocyclic ligands usually exhibit two intense bands ($\epsilon \geq 10^3$) in the 500-400 nm region together with very intense charge-transfer bands in the ultraviolet region (32,80,81). These bands are easily distinguished in the spectrum of $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$ (Fig. 8). The nature of the electronic transitions which give rise to the two lower energy bands is a subject of great debate, and arguments in support of both d-d (81) and Co-C charge-transfer (80) transitions

have been presented. This question remains unresolved and is not of importance here.

In comparing the spectra of the two complexes major differences are observed in the visible region while the spectra are qualitatively similar in the ultraviolet region. This agrees with the macrocyclic ligand origin of the UV bands. The low energy band observed in the spectrum of the dimethyl complex is somewhat unsymmetrical to the high energy side and may indicate the presence of an obscured second visible band. This effect has been observed for other alkyl cobalt complexes (80). The high energy positions of these bands relative to those of the monomethyl complex is consistent with the superior σ -donor character of CH_3^- relative to H_2O . The energies of the visible bands of most monoalkylcobalt complexes depend similarly on the σ -donor power of the axial and chelating ligands (80,81).

NMR Spectra. The ^1H -NMR spectra of $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ and $(\text{CD}_3)_2\text{Co}(\text{BDM1,3pn})$ were recorded in CDCl_3 and DMSO-d_6 for the purposes of identification, and to confirm the assignments made by Pellizer et al., (61) especially with regard to the position of the axial methyl protons.

The NMR spectrum of $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ is shown in Figure 9 and the spectral data are summarized in Table VI. The proton signals due to the equivalent axial methyl groups appear as a sharp singlet at 0.07 ppm.

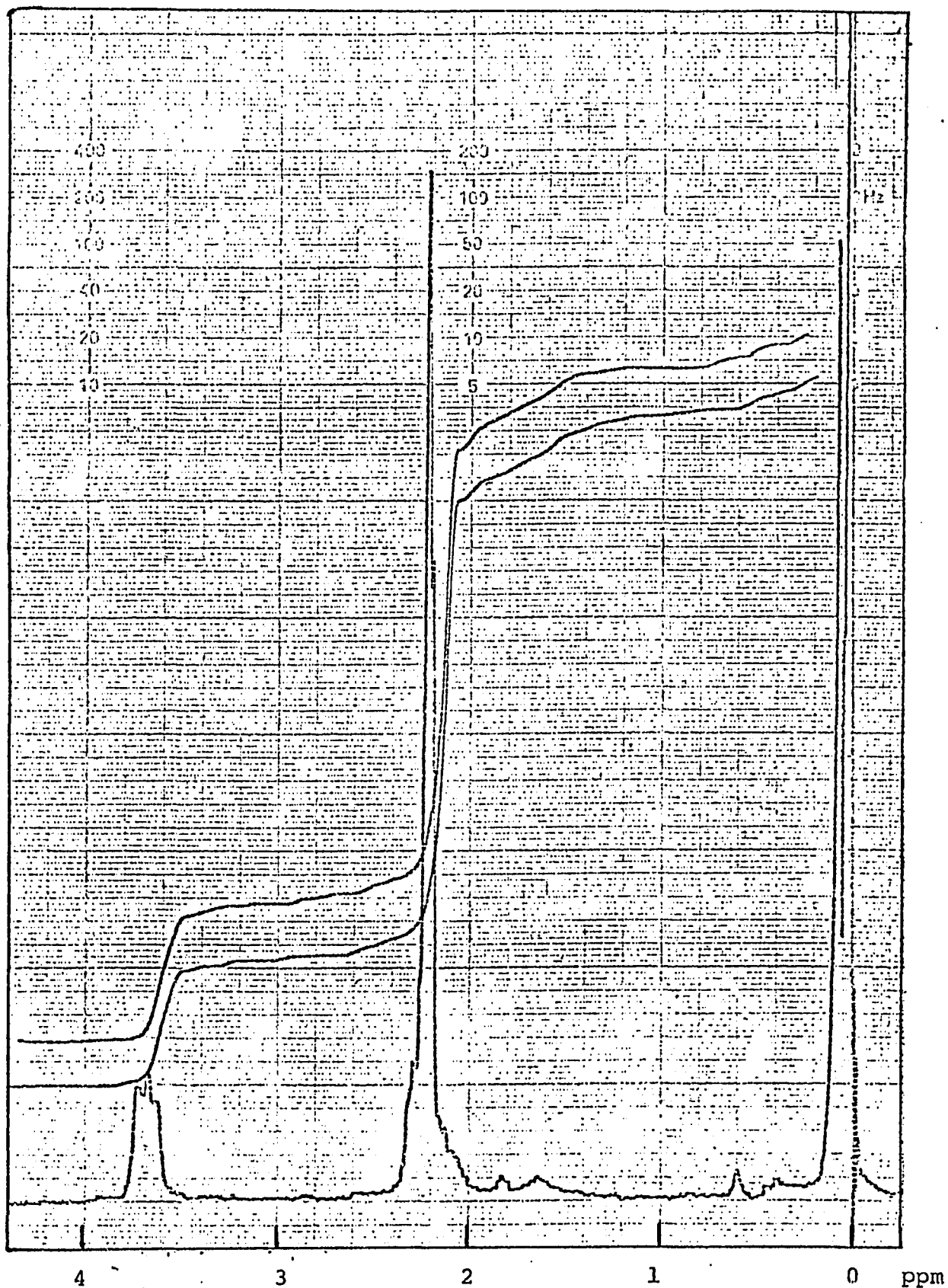


Fig. 9. ^1H -NMR Spectrum of $(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$

Table VI. ^1H -NMR Spectral Data in DMSO-d_6 .

<u>Complex</u>	<u>Chemical Shift, ppm^a</u>		<u>Multiplicity</u>	<u>Assignment</u>
$(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$	0.07	(2)	singlet	Co-CH_3
	2.20	(14)	singlet	$\text{N} = \text{C-CH}_3$
	2.22		singlet	
	2.0-2.3		multiplet	$\text{C-CH}_2\text{-C}$
	3.70	(4)	triplet	N-CH_2
$(\text{CD}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$	2.20	(14)	unresolved singlet	$\text{N} = \text{C-CH}_3$
				$\text{C-CH}_2\text{-C}$
	3.65	(4)	triplet	N-CH_2

^a() = Relative integrated area.

This assignment is confirmed by the spectrum of $(\text{CD}_3)_2\text{Co}(\text{BDML},3\text{pn})$ (Fig. 10), which does not exhibit a signal at this position; and is in agreement with the value of 0.06 ppm reported previously (61). The high field position of this signal confirms that these methyl groups are bound directly to cobalt, since $\text{Co}-\text{CH}_3$ signals between 0 and 1 ppm are typical for other dimethylcobalt chelates (36). For example, the axial methyl resonance positions of $[(\text{CH}_3)\text{Co}(\text{tim})]^+$ and $[(\text{CH}_3)_2\text{Co}(\text{CR})]^+$ are observed at 0.36 and 0.18 ppm respectively.

The small variation in position of the $\text{Co}-\text{CH}_3$ signals seen for the dimethylcobalt complexes presumably reflects the variations of electron density on cobalt due to the different electron donor propensities of the macrocyclic ligands. Thus, the order of increasing resonance field $\text{tim} < \text{CR} < \text{BDML},3\text{pn}$ is in agreement with the increasing electron donor character of the ligands in the same order, as obtained from polarographic and electronic spectral data (81). The same explanation of increased electron density on cobalt can be invoked to account for the high field position (-1.56 ppm) of the $\text{Co}-\text{CH}_3$ resonance of $[\text{CH}_3\text{Co}^{\text{I}}(\text{tim})]$ (36).

The assignments of the remaining signals were made on the basis of the integrated areas, and on the known NMR spectrum of $[\text{CH}_3\text{Co}(\text{BDML},3\text{pn})\text{H}_2\text{O}]\text{ClO}_4$ (82). The relative areas in the spectrum of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ verify that there are two methyl groups bound to cobalt.

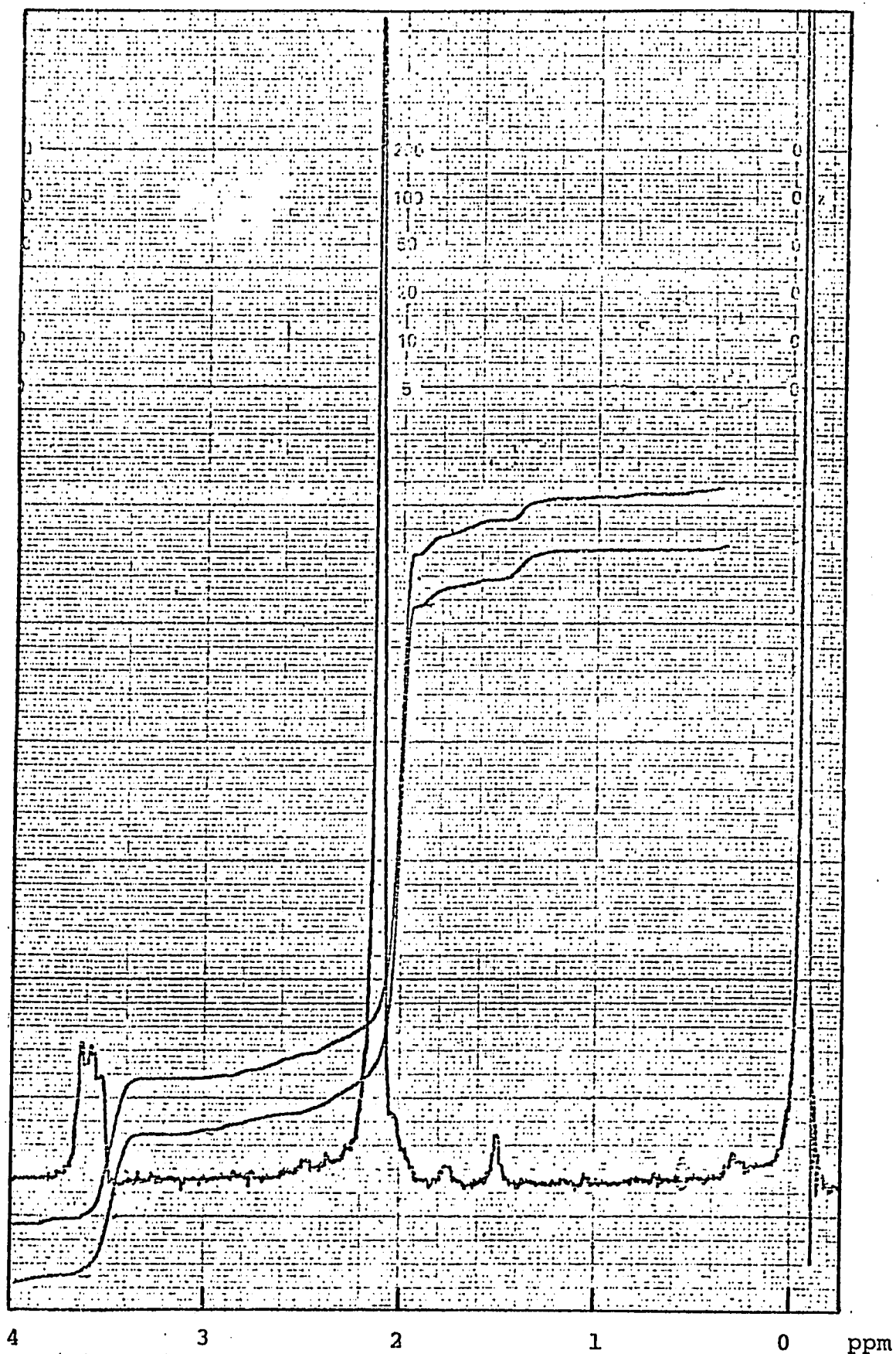


Fig. 10. ^1H -NMR Spectrum of $(\text{CD}_3)_2\text{Co}(\text{BDM1,3pn})$

These measurements were made in TMS-free DMSO due to proximity of the Co-CH₃ signal to that of TMS.

Infrared Spectra. The infrared spectra of (CH₃)₂Co(BDML,3pn) and (CD₃)₂Co(BDML,3pn) were recorded as Nujol and halocarbon mulls in the 4000-200 cm⁻¹ region in an attempt to identify the expected stretching $\nu(\text{Co-CH}_3)$, deformation $\delta(\text{Co-CH}_3)$, and rocking $\rho(\text{Co-CH}_3)$ vibrational modes of the cobalt-bonded methyl groups. The IR spectrum of the non-alkyl complex [Co(BDML,3pn)-Br₂] was also recorded to aid in the identification of the frequencies associated with the macrocyclic ligand BDML,3pn. The pertinent data are presented in Table VII.

The results of these experiments are somewhat disappointing since only the cobalt-carbon bond stretching vibration was identified. Table VII shows that the spectra of [Co(BDML,3pn)Br₂] and (CH₃)₂Co(BDML,3pn) are very similar. The strong absorption bands in the 430-540 cm⁻¹ region are presumably attributable to Co-N bond vibrations, since similar absorption bands have been observed in the IR spectra of cobaloximes (83). The slightly higher frequencies observed for the dimethyl complex reflects the superior σ -donor character of CH₃ relative to Br (61). This causes an increase in electron density on the cobalt atom, thereby facilitating the back donation of electrons from the d-orbitals of cobalt to the nitrogen atoms of BDML,3pn. This results in a stronger Co-N bond and a high frequency shift of the

Co-N vibrations.

Of particular interest is the strong and broad absorption band at 488 cm^{-1} found in the spectrum of $(\text{CH}_3)_2\text{Co}(\text{BDM1},3\text{pn})$. This band was tentatively assigned to the stretching vibration of the Co-C bond since only a weak band at 475 cm^{-1} was observed in the spectrum of $[\text{Co}(\text{BDM1},3\text{pn})\text{Br}_2]$. In order to prove this assignment the spectrum of $(\text{CD}_3)_2\text{Co}(\text{BDM1},3\text{pn})$ was recorded. The replacement of the cobalt-bonded methyl groups by methyl- d_3 resulted in a new band at 467 cm^{-1} ; and a decrease in intensity and sharpening-up of the band at 488 cm^{-1} . Although $\nu(\text{Co-CH}_3)$ does not fall by the expected factor of $(15/18)^{1/2}$ (42 cm^{-1}) upon deuteration, a low frequency shift of 21 cm^{-1} is observed. This discrepancy between the experimental and calculated isotopic shift can be explained in terms of the coupling of the Co-C stretching vibration with the Co-N vibrations of the molecule.

Additional support for the assignment of the 488 and 467 cm^{-1} bands as the cobalt-carbon stretching frequencies is obtained from experiments with monomethylcobaloxime complexes of the type $[\text{CH}_3\text{Co}(\text{dmg})_2\text{B}]$ (84). The IR spectra of these complexes show a definite relationship between the position of $\nu(\text{Co-CH}_3)$, and the electron donating power of the axial base. These vibrations occur in the $320\text{--}340\text{ cm}^{-1}$ region and move to

higher frequency as the donor power of the base increases. Thus, the relatively high frequency position of $\nu(\text{Co-CH}_3)$ observed in the spectrum of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ is consistent with the superior σ -donor strength of CH_3 . Finally, several of the dimethyl complexes discussed in a previous section (i.e. $(\text{CH}_3)_2\text{Co}(\text{acac})(\text{PR}_3')_2$, $(\text{CH}_3)_2\text{Co}(\text{bipy})_2$ etc.) show cobalt-carbon bond stretching frequencies in the $390\text{--}500\text{ cm}^{-1}$ range (51,55). These frequencies agree quite well with the values of 488 cm^{-1} and 467 cm^{-1} found here for $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ and $(\text{CD}_3)_2\text{Co}(\text{BDML},3\text{pn})$.

Several characteristic bands appear rather consistently in the $2000\text{--}700\text{ cm}^{-1}$ range, however the sought after $\delta(\text{Co-CH}_3)$ and $\rho(\text{Co-CH}_3)$ vibrational modes were not found presumably because of strong ligand bands in the regions of interest. All of the complexes show a weak broad band between 1780 and 1770 cm^{-1} which is attributable to the intramolecular hydrogen bridge of $\text{BDML},3\text{pn}$. This conclusion is supported by the presence of similar bands in the IR spectra of cobaloximes (83) and the absence of these bands in the spectra of the corresponding sodium salts (85). The prominent band observed in the vicinity of 1500 cm^{-1} is attributed to the C=N stretching frequency. Burger et al. (85) reported that lower C=N vibrational frequencies are observed as the strength of the $\text{M} \longrightarrow \text{N=C } \pi\text{-bond}$ increases for a series of cobaloximes. The order of $\nu(\text{C=N})$

Table VII. Characteristic IR Absorption Bands of Complexes Studied (cm^{-1}).

<u>Complex</u>	<u>δ (O-H O)</u>	<u>ν (C=N)</u>	<u>δ (CH_3)_{as}</u>	<u>δ (CH_3)_s</u>	<u>ν (N-O)_{as}</u>
Co (BDML, 3pn) Br ₂	1780 (w)	1520 (s)	1430 (m)	1370 (m)	1210 (m)
(CH ₃) ₂ Co (BDML, 3pn)	1775 (w)	1465 (s)	1430 (m)	1370 (m)	1245 (s)
(CD ₃) ₂ Co (BDML, 3pn)	1775 (w)	1465 (s)	1430 (m)	1370 (m)	1245 (s)
	ν (N-O) _s	δ (OH)	δ (C=N-O)		
Co (BDML, 3pn) Br ₂	1110 (m)	880 (m)	740, 720 (m)		
(CH ₃) ₂ Co (BDML, 3pn)	1120 (m)	865 (m)	740, 710 (m)		
(CD ₃) ₂ Co (BDML, 3pn)	1120 (m)	865 (m)	740, 710 (m)		
<hr/>					
w = weak, m = medium, s = strong					

Table VII. (Cont).

Complex	$\nu(\text{Co-N})$	$\nu(\text{Co-N})$	$\nu(\text{Co-CH}_3)$ $\nu(\text{Co-N})$	$\nu(\text{Co-CD}_3)$	$\nu(\text{Co-N})$
$\text{Co}(\text{BDML}, 3\text{pn})\text{Br}_2$	530(s)	515(s)	475(w)	-	436(s)
$(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$	542(s)	518(s)	488(s) broad	-	447(s)
$(\text{CD}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$	541(s)	519(s)	486(m) sharp	486(w)	447(s)

w = weak, m - medium, s = strong

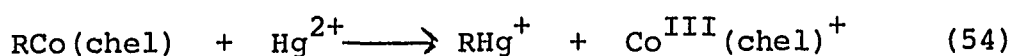
$[\text{Co}(\text{BDML},3\text{pn})\text{Br}_2] > (\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn}) = (\text{CD}_3)_2\text{Co}(\text{BDML},3\text{pn})$, is consistent with this interpretation since Br has empty d-orbitals of appropriate symmetry which can compete for the π -electron density of cobalt, thereby weakening the Co-N bond.

There are two bands of medium intensity which appear at identical frequencies (1430 and 1370 cm^{-1}) in the spectra of all three complexes. These bands are due to asymmetric and symmetric deformation vibrations of the methyl groups in BDML,3pn. On the basis of experiments by Blinc and Hadzi (86) the bands in the vicinity of 1245 and 1120 cm^{-1} were assigned to the N-O stretching vibrations. The bands around 880-860 cm^{-1} may be attributed to deformation vibrations of OH in BDML,3pn and the bands around 740 cm^{-1} to C=N-O deformation vibrations. Additional bands were observed which are presumably due to C-C, C-N and C-H vibrations, however these will not be discussed here.

Reactions of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$

Reactions in which alkyl groups are transferred from synthetic monoalkylcobalt complexes to metal electrophiles have been the subject of intensive investigations in recent years. Interest in these reactions has been heightened by the probable biosynthetic role of methylcobalamin in the conversion of inorganic mercury

to highly toxic methyl mercury compounds in lake and river sediments under environmental conditions (9). The reactions of alkylcobaloximes with Hg^{2+} have been the most studied in this respect (87-89), although analogous reactions with Cr^{2+} (90) and Tl^{3+} (91) have been reported. More recently, the reactions of $[\text{RCoL}^*(\text{H}_2\text{O})]^+$ (68,92) and of $\text{CH}_3\text{Co}(\text{chel})$ ($\text{chel} = \text{tim}$, salen and saloph) (93) with Hg^{2+} were studied in detail. These reactions invariably exhibit a 1:1 stoichiometry and result in the products shown in (Eqn. 54).



Despite the ready cleavage of the Co-C bond by Hg^{2+} , Cr^{2+} , and Tl^{3+} a surprising number of other electrophilic reagents including H_3O^+ , CH_3Hg^+ , Zn^{2+} , Cd^{2+} , Pb^{2+} and Al^{3+} are unreactive toward monoalkylcobalt chelates (94,95). Consequently, we became interested in studying the reactions of the trans-dimethyl complex $(\text{CH}_3)_2\text{CoL}$ with selected metal electrophiles, especially following earlier studies with monomethyl complexes which established the superior σ -donor and trans labi-

*L will be used as an abbreviation for $\text{BDML}, 3\text{pn}$ in this section to simplify the discussion.

lizing character of CH_3 relative to other Lewis bases (17,96). Our thinking in this regard was that one methyl group would be extremely susceptible to electrophilic attack, and that methyl-transfer reactions with previously unreactive electrophiles might be made to occur. Of particular interest were the reactions with Zn^{2+} , Cd^{2+} and Pb^{2+} in view of the current concern about pollution by these metals (97,98).

In this section the reactions of $(\text{CH}_3)_2\text{CoL}$ with Zn^{2+} , Cd^{2+} and Pb^{2+} in $i\text{-C}_3\text{H}_7\text{OH}$ are discussed. These reactions are significant since they represent the first examples of alkyl-transfer from an organocobalt complex to these metal ions. In addition, the reactions with H_3O^+ , Ag^+ , light, and heat will be discussed. The products of these reactions are summarized in Figure 11.

Stability of $(\text{CH}_3)_2\text{CoL}$ in Solution

In order to investigate the reactions of $(\text{CH}_3)_2\text{CoL}$ with H_3O^+ and metal electrophiles an appropriate medium had to be found in which the complex was stable. Consequently, kinetic measurements were made on the decomposition reactions of $(\text{CH}_3)_2\text{CoL}$ in a variety of solvents including tetrahydrofuran, acetone, water, methanol, ethanol, and 2-propanol. These reactions were carried out in the dark to avoid decomposing the complex

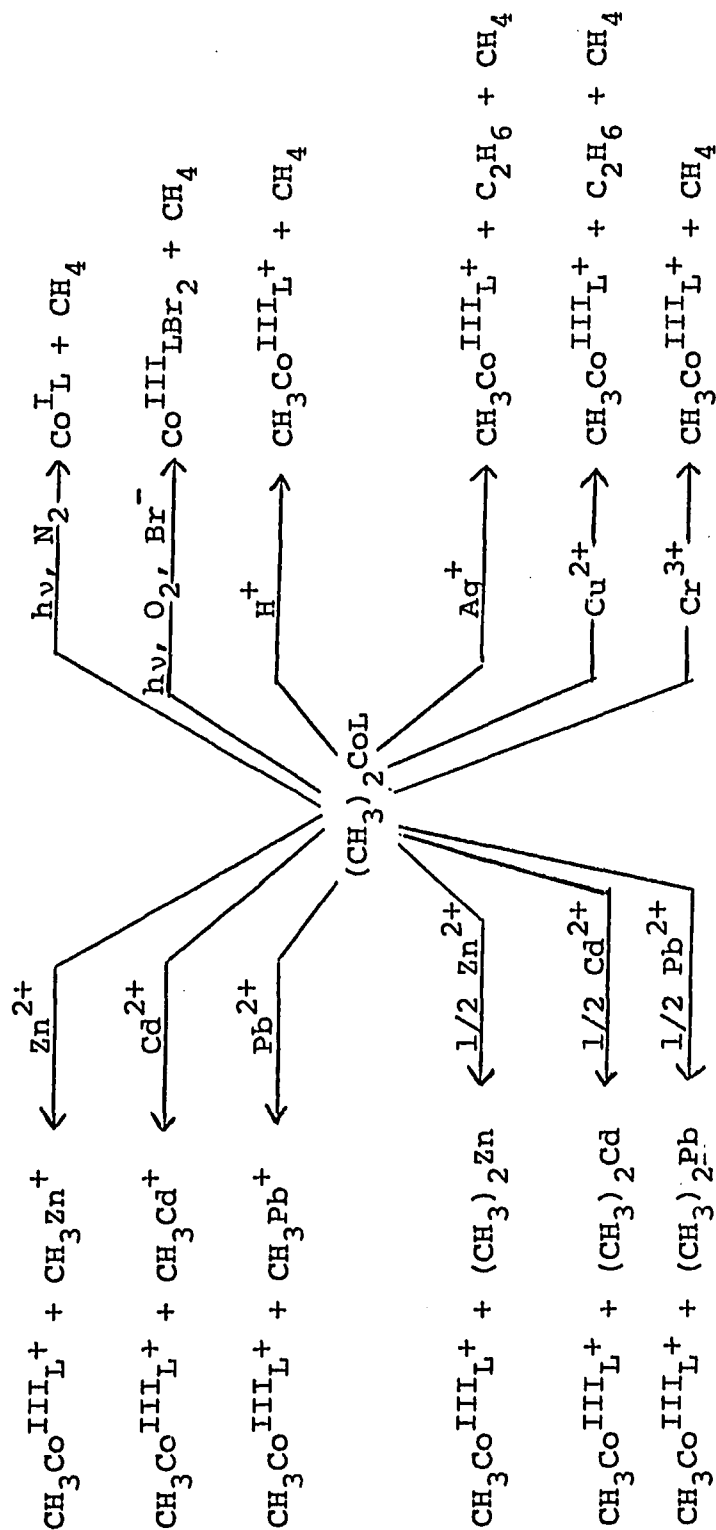
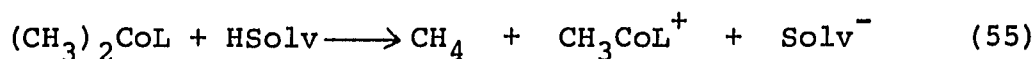


Fig. 11. A Summary of the Reactions of $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$.

photochemically.

The stability of $(\text{CH}_3)_2\text{CoL}$ in solution is quite variable due to the reaction of the complex with acidic protons of the solvent. The products of these reactions invariably are CH_4 and the corresponding monomethyl complex (Eqn. 55). The alkane was identified by GLC,



and the monomethyl complex identified by spectrophotometric comparison to a solution containing an analyzed sample of $[\text{CH}_3\text{CoL}(\text{H}_2\text{O})]\text{ClO}_4$.

The rate of decomposition $(\text{CH}_3)_2\text{CoL}$ was monitored spectrophotometrically by observing the decrease in absorbance at 412 nm or the increase in absorbance at 460 nm (Fig. 12). The presence of isosbestic points at 490 and 450 nm indicated that only one product was formed in solution. The rate data (APPENDIX I) follow the pseudo-first-order rate law (Eqn. 56) in all cases

$$\frac{-d[(\text{CH}_3)_2\text{CoL}]}{dt} = k_{\text{obs}}[(\text{CH}_3)_2\text{CoL}] \quad (56)$$

since plots of $\ln(A-A_\infty)$ versus time were linear over several half-lives as shown for H_2O and CH_3OH in Figure 13.

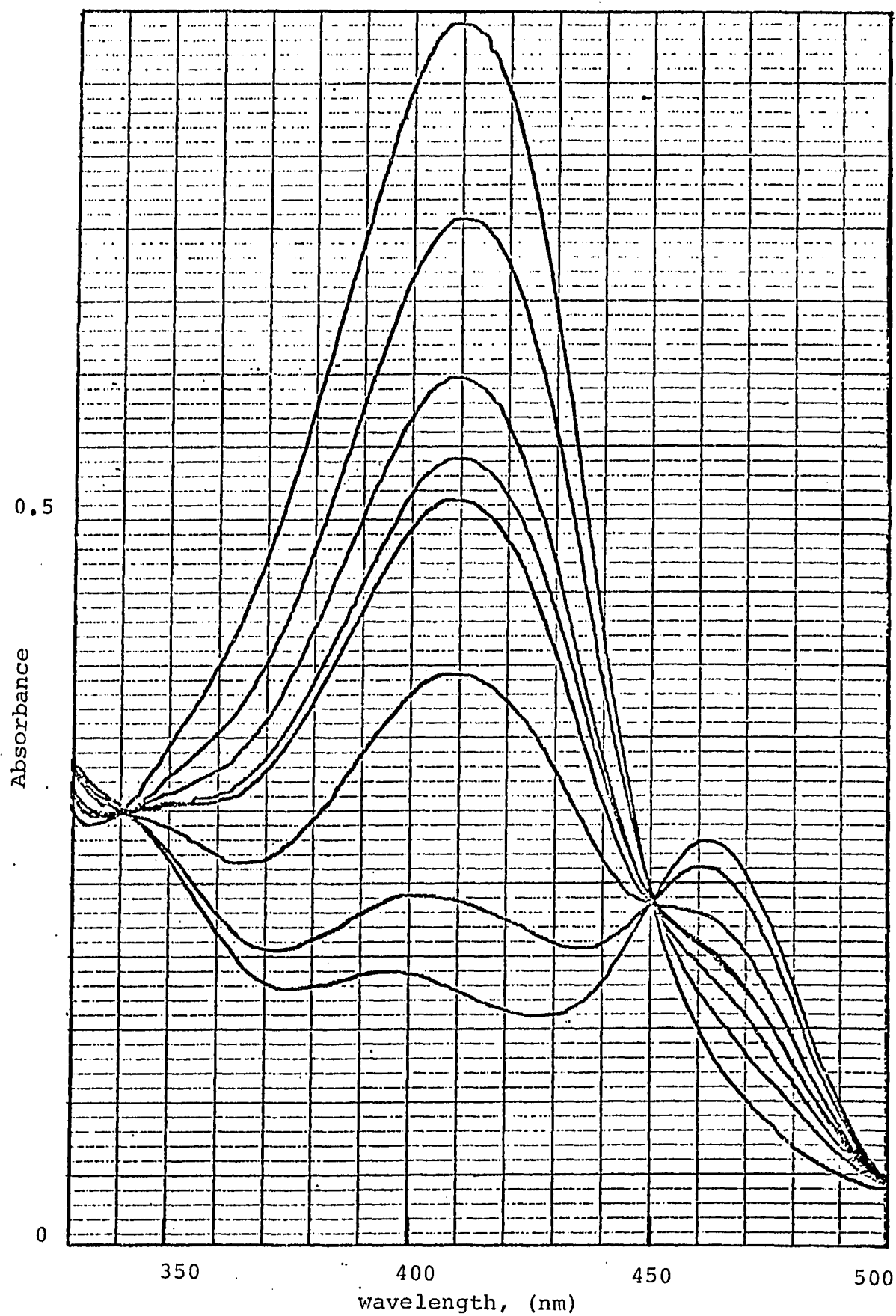


Fig. 12. Decomposition of $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ in 2-propanol.

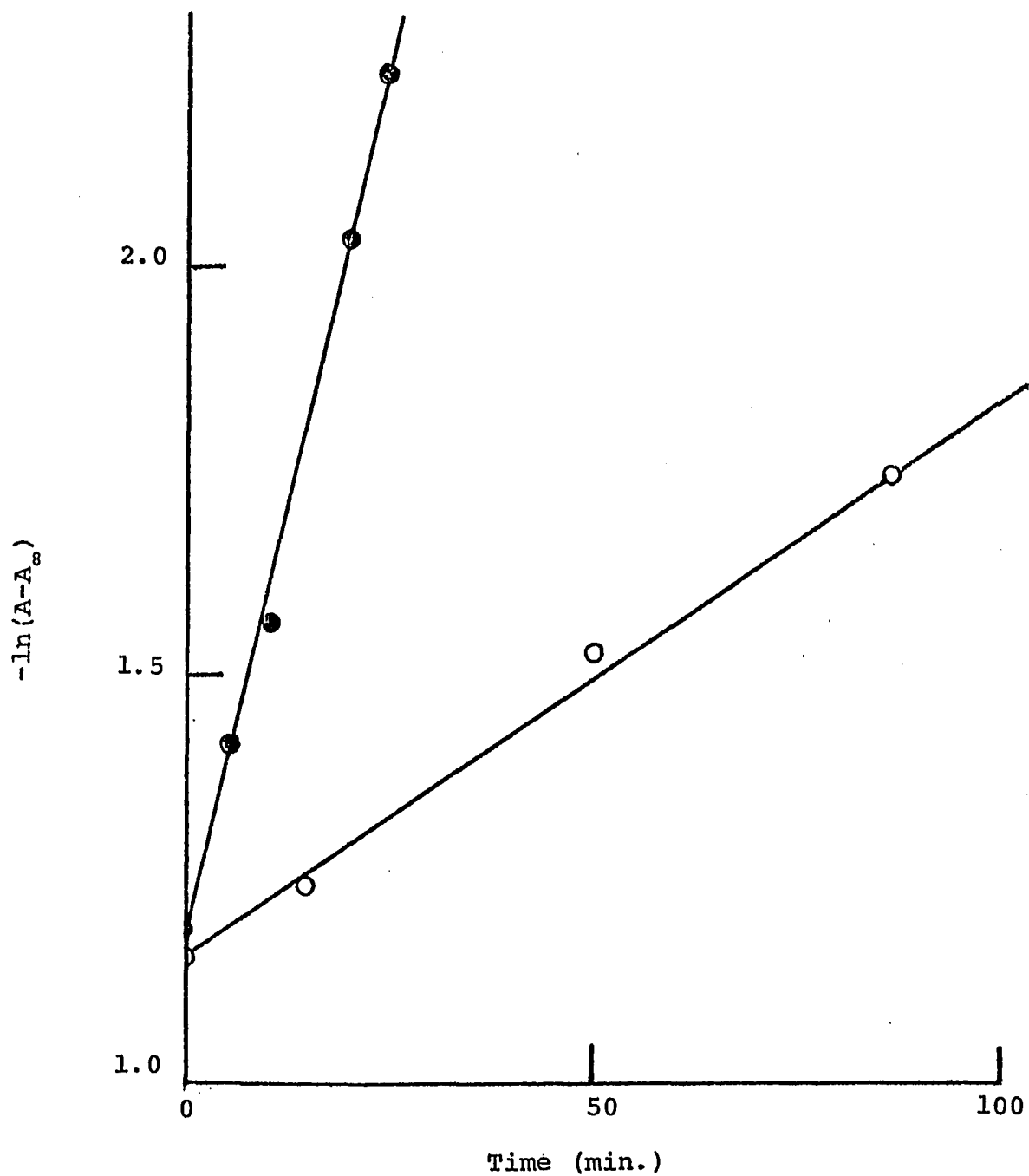
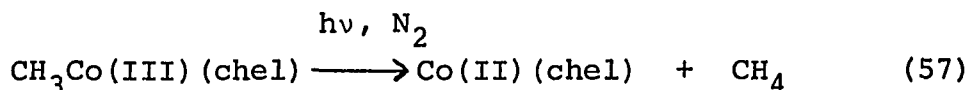


Fig. 13. Representative Plots of $\ln(A-A_\infty)$ Versus Time for the Decomposition of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ in Solution; H_2O , ●; CH_3OH , ○.

A summary of the kinetic data for the decomposition of $(\text{CH}_3)_2\text{CoL}$ in the solvents investigated is presented in Table VIII. The observed anaerobic stability order is: tetrahydrofuran = acetone > $i\text{-C}_3\text{H}_7\text{OH}$ > $\text{C}_2\text{H}_5\text{OH}$ > CH_3OH > H_2O . This order agrees with the acidity of the solvents which increases in the order: $i\text{-C}_3\text{H}_7\text{OH}$ < $\text{C}_2\text{H}_5\text{OH}$ < CH_3OH < H_2O (99). The aprotic solvents tetrahydrofuran and acetone do not contain acidic hydrogens and as a consequence $(\text{CH}_3)_2\text{CoL}$ is relatively stable in these solvents. The presence of oxygen does not affect the stability of $(\text{CH}_3)_2\text{CoL}$ in these solvents in the dark.

Photolysis of $(\text{CH}_3)_2\text{CoL}$

Several papers (28,29,80) have been published on the photolysis of organocobalt chelates RCo(III)(chel)^* , where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$, etc. The reactions of solutions of $\text{CH}_3\text{Co(III)(chel)}$ with light yield predominantly CH_4 as the organic product, and Co(II)(chel) or Co(III)(chel) (Eqns. 57 and 58). A study of the photolysis of



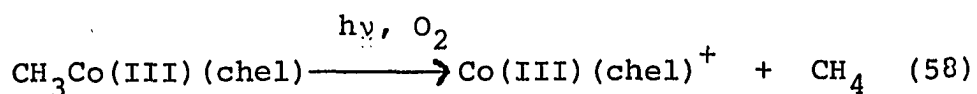
*chel = a generalized chelating ligand; see for example (Fig. 3).

Table VIII. The Half-Life and k_{obs} Values for the
Decomposition of $(\text{CH}_3)_2\text{Co}(\text{BDM}1,3\text{pn})$ in
Various Solvents at Room Temperature.^a

<u>Solvent</u>	<u>half-life (min)</u>	<u>k_{obs} (min^{-1})</u>
tetrahydrofuran	stable ^b	-
acetone	stable ^b	-
$i\text{-C}_3\text{H}_7\text{OH}$	12,550	5.52×10^{-5}
$\text{C}_2\text{H}_5\text{OH}$	305	2.27×10^{-3}
CH_3OH	94	7.39×10^{-3}
95% aqueous $\text{C}_2\text{H}_5\text{OH}$	103	6.75×10^{-3}
H_2O	17	4.08×10^{-2}

^aIn the absence of light and oxygen.

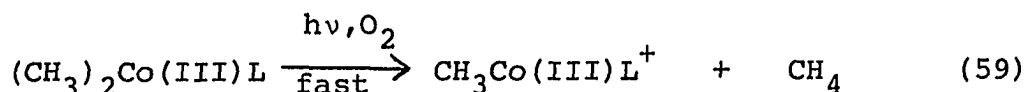
^bNo significant decomposition in 18 hr.

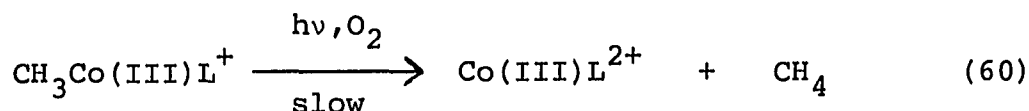


$(\text{CH}_3)_2\text{CoL}$ was initiated primarily to determine how sensitive the complex was to light, although it was also of interest to compare the photochemical reactions of the dimethyl complex to those of the corresponding monomethylcobalt chelate $[\text{CH}_3\text{CoL}(\text{H}_2\text{O})\text{ClO}_4]$.

Solution Photolysis. Preliminary reactions were carried out in CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$ in the presence and absence of oxygen. As with the majority of organocobalt(III) compounds $(\text{CH}_3)_2\text{CoL}$ is very sensitive to light in solution and decomposes even in the diffuse light of the laboratory. Upon irradiating solutions of $(\text{CH}_3)_2\text{CoL}$ with light, color changes were readily apparent after several minutes of illumination. Consequently, these reactions were monitored most conveniently by observing the disappearance of the visible maximum at 412 nm which is characteristic of $(\text{CH}_3)_2\text{CoL}$ (Table V).

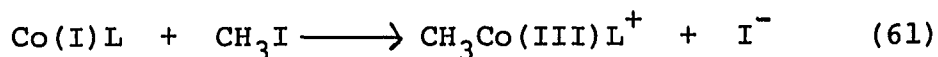
During aerobic photolysis a two-step reaction is observed (Eqns. 59 and 60). The first step is faster



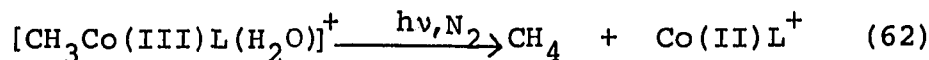


since a peak at 460 nm due to $\text{CH}_3\text{Co(III)L}^+$ is formed, but the two steps overlap resulting ultimately in the products shown in equation 60. The final Co(III)L^{2+} product was converted to $[\text{Co(III)LBr}_2]$ by the addition of excess $(\text{N-C}_4\text{H}_9)_4\text{Br}$, and the dibromide complex identified by its visible maximum at 300 nm (Table V).

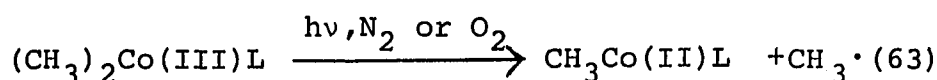
The anaerobic photolysis of $(\text{CH}_3)_2\text{CoL}$ resulted in a very different reaction. Although CH_4 was the only organic product formed in analogy to the aerobic reactions, all three solutions showed an intense blue-green coloration upon exhaustive photolysis. This color was attributed to the formation of Co(I)L since: (1) the visible spectrum showed the characteristic absorption of Co(I)L at 665 nm (Table V), and (2) the blue-green product reacted rapidly with CH_3I to yield orange $\text{CH}_3\text{Co(III)L}^+$ (Eqn. 61). At no time during the



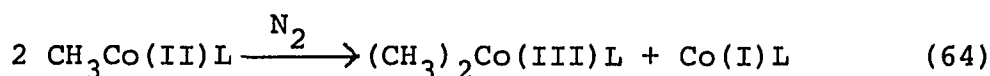
course of these reactions was Co(II)L^+ or $[\text{CH}_3\text{Co(I)L}^-]$ observed spectrophotometrically (Table V). The former product was identified upon exhaustive anaerobic photolysis of $[\text{CH}_3\text{Co(III)L(H}_2\text{O)}]\text{ClO}_4$ in $i\text{-C}_3\text{H}_7\text{OH}$ however (Eqn. 62).



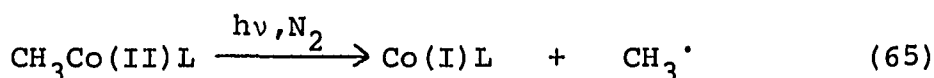
The products of the above anaerobic and aerobic photolysis reactions of $(\text{CH}_3)_2\text{CoL}$ can be explained by a process in which both Co-C bonds are cleaved homolytically in a step-wise fashion. In the first step the homolysis of one Co-C bond yields a methyl radical and unstable $\text{CH}_3\text{Co(II)L}$ (Eqn. 63). Under anaerobic con-



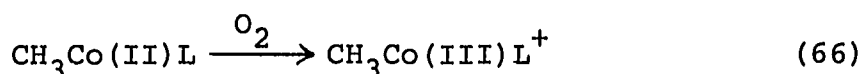
ditions the $\text{CH}_3\text{Co(II)L}$ species rapidly disproportionates into $(\text{CH}_3)_2\text{CoL}$ and Co(I)L (Eqn. 64). The resulting



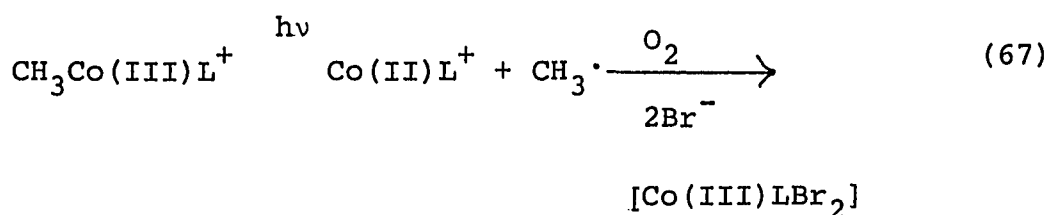
dimethyl complex then photolyzes according to equation 63 and the cycle continues until ultimately Co(I)L is the only product observed. The disproportionation of $\text{CH}_3\text{Co(II)L}$ after its electrolytic production in DMF was observed by Costa, Puxeddu, and Reisenhofer (39,100) which agrees with the mechanism proposed here. However, the photolysis of $\text{CH}_3\text{Co(II)L}$ according to equation 65 cannot be completely ruled out.



In the aerobic reaction the transient $\text{CH}_3\text{Co(II)L}$ species formed in the first step (Eqn. 63) is rapidly oxidized by oxygen in preference to its disproportionation (Eqn. 66). This explains the formation of



$\text{CH}_3\text{Co(III)L}^+$ in these reactions (Eqn. 59). Finally, in a somewhat slower reaction the intermediate $\text{CH}_3\text{Co(III)L}^+$ species is photolyzed to Co(II)L^+ which rapidly reacts with oxygen to yield the ultimate Co(III)L^{2+} product (Eqn. 67). This final reaction was



confirmed by aerobically photolyzing an analyzed sample of $[\text{CH}_3\text{Co(III)L(H}_2\text{O)ClO}_4]$ in 2-propanol and identifying the Co(III)L^{2+} product spectrophotometrically. Although the Co(II)L^+ species was not detected by spectrophotometric means this does not preclude its transient existence.

The methyl radicals which are liberated upon homolysis of the Co-C bonds (Eqns. 63 and 67) could conceivably react by one of several routes: (1) abstract a hydrogen atom from either the solvent or ligand to form methane, (2) dimerize to form ethane, (3) abstract a methyl group from the ligand to form ethane, or (4) react with O_2 to form formaldehyde. The exclusive formation of CH_4 as the organic product (confirmed by GLC analysis) in both the anaerobic and aerobic reactions precludes (2), (3) and (4) as possibilities, and these were not considered further. It seems likely that the methyl radicals abstract the α -hydrogen atoms of the alcohols since a seven line electron paramagnetic resonance (EPR) spectrum due to $(CH_3)_2\dot{C}OH$ was observed upon photolyzing $CH_3Co(dmgl)_2Py$ in $i-C_3H_7OH$ (101). Further support for this mechanism in the present work comes from a study of the rates of photolysis.

The rates of the above aerobic and anaerobic photodecomposition reactions of $(CH_3)_2CoL$ were measured in anhydrous CH_3OH , C_2H_5OH , and $i-C_3H_7OH$. For the anaerobic reactions in C_2H_5OH and $i-C_3H_7OH$ the rate data (APPENDIX II) conform quite well to the first-order rate law (Eqn. 56), since plots of $\ln(A-A_\infty)$ versus time were linear over several half-lives. The observed rate constants (k_{obs}) and half-lives ($t_{1/2}$) were determined from the slopes of these lines and are summarized in

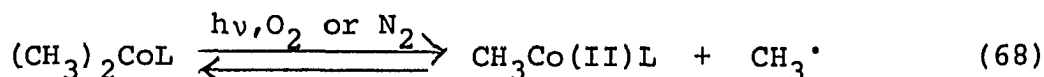
Table IX. Comparative data with CH_3OH could not be obtained, however, because of the importance of the acidic reaction which yields $\text{CH}_3\text{Co(III)L}^+$ and CH_4 (see Eqn. 55).

Table IX. Kinetic Data for the Anaerobic Photolysis of $(\text{CH}_3)_2\text{CoL}$

Solvent	$k_{\text{obs}} (\text{min}^{-1})$	$t_{1/2} (\text{min})$
$\text{C}_2\text{H}_5\text{OH}$	0.020	34.5
$i\text{-C}_3\text{H}_7\text{OH}$	0.043	16.1

The photolysis rate in each alcohol was considerably faster in the presence of O_2 ; the reactions being completed in less than 10 minutes in all three solvents. Plots of $\ln(A-A_\infty)$ versus time were not linear however, indicating that a more complicated rate law is operative in these reactions. Although these results are interesting from a kinetic point of view, these reactions were not studied further.

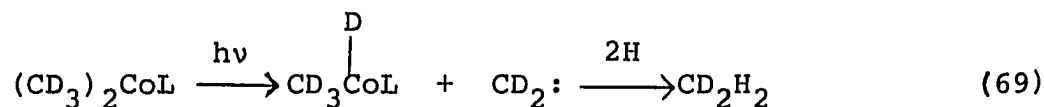
The relative rates of aerobic $\gg i\text{-C}_3\text{H}_7\text{OH} > \text{C}_2\text{H}_5\text{OH}$ can be explained by considering the fate of the radical $\text{CH}_3\text{Co(II)L}$ and CH_3^\cdot products formed in the rate determining step (Eqn. 68). If no easily abstracted



hydrogen or radical scavenger is available, the reverse of equation 68 becomes important and the reaction rate slows (29,80). However, any species including O_2 that reacts with the products increases the reaction rate. Thus, in the anaerobic reaction the relative rates $i\text{-C}_3\text{H}_7\text{OH} > \text{C}_2\text{H}_5\text{OH}$ parallel the ease of abstraction of the α -hydrogen of the alcohol by the methyl radical (102,103). Analogous results were obtained during the anaerobic photolysis of methylcobalamin in $i\text{-C}_3\text{H}_7\text{OH}$ and $\text{C}_2\text{H}_5\text{OH}$ (104). In fact the reaction in $i\text{-C}_3\text{H}_7\text{OH}$ was faster by a factor of 2.4 which is nearly identical to the factor of 2.2 observed in this work. The accelerating effect of O_2 is explained in terms of its rapid reaction with $\text{CH}_3\text{Co(II)L}$ to yield $\text{CH}_3\text{Co(III)L}^+$ (Eqn. 66), thus decreasing the importance of the recombination reaction.

Mass spectral analysis of the alkane formed during the anaerobic photolysis of $(\text{CH}_3)_2\text{CoL}$ corroborates the conclusion of a homolytic process. The only observed alkane product (CD_3H) is consistent with the formation of a CD_3^\cdot intermediate and not a carbene intermediate which would be expected if an α -elimination

process (Eqn. 69) were a competing reaction.



The analysis was not straight forward however, and some of the problems encountered will now be discussed.

Initially, CD_3H was prepared by the acid hydrolysis of $(\text{CD}_3)_2\text{CoL}$ in $i\text{-C}_3\text{H}_7\text{OH}$ (see Reaction with H_3O^+) and its mass spectrum recorded using an electron energy of 75 eV. It soon became apparent that the analysis was going to be more difficult than expected since a very complicated spectrum was obtained with a considerable amount of fragmentation in the region below m/e 45. A comparison of this spectrum to that of pure $i\text{-C}_3\text{H}_7\text{OH}$ confirmed our suspicions, i.e. the vapor pressure of $i\text{-C}_3\text{H}_7\text{OH}$ was sufficiently high at room temperature to interfere with the desired spectrum of CD_3H . This problem was solved by cooling the reaction flask to -78°C in a dry-ice acetone bath.

A second problem encountered was that any analysis of a mixture of CD_3H (m/e 19) and CD_2H_2 (m/e 18) would be complicated by the presence of background H_2O (m/e 18) and fragment peaks such as CD_3^+ (m/e 18). This problem is exemplified by the high resolution spectrum of CD_3H (Fig. 14) in the region m/e 18-19. Three peaks are observed; an intense singlet at m/e 18

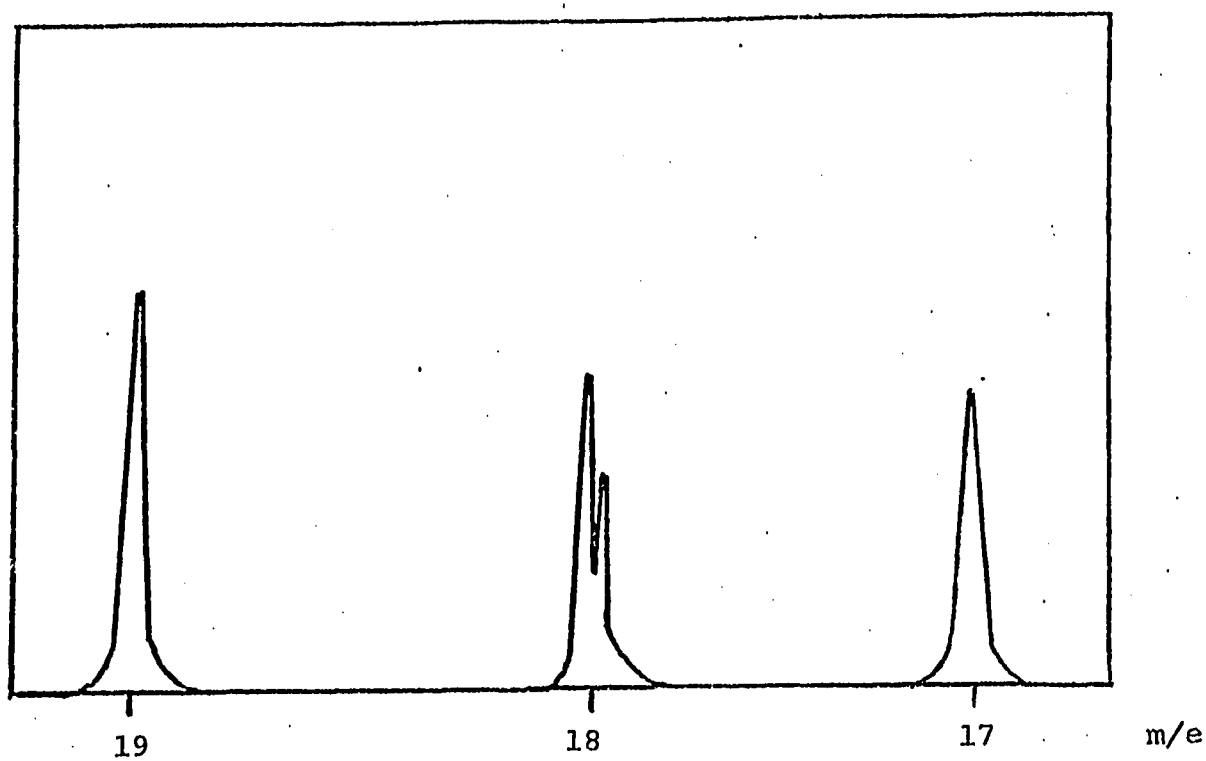


Fig. 14. High Resolution Mass Spectrum of CD_3H (m/e 19-17),
50eV.

due to CD_3^+ , and a doublet at m/e 18. The lower mass peak of the doublet was assigned to H_2O^+ (m/e 18.011) since the addition of H_2O caused a marked increase in the intensity of this peak. The higher mass peak was assigned to CD_3^+ by measuring the distance (mm) from H_2O^+ (m/e 18.011) to CD_3H^+ (m/e 19.050), and calculating the factor 0.017 (m/e)/mm. Multiplication of this factor by the distance from H_2O^+ (m/e 18.011) to the unknown peak gave the unknown mass ($m/e = 18.040 \pm 0.001$). This corresponds quite closely to that expected for CD_3^+ (m/e 18.042).

In order to solve the problems discussed above, the spectra were simplified using low-voltage mass spectrometry. In this method the spectrum is determined at an electron energy (10-15 eV) sufficient for the production of molecular ions, but not the corresponding fragments (105). The optimal electron energy (10 eV) for the present analysis was chosen empirically by repeatedly scanning the mass spectrum of CD_3H while stepwise decreasing the potential from a high 75 eV. A solution of $(\text{CD}_3)_2\text{CoL}$ was then photolyzed and the mass spectrum of the liberated methane recorded at 10 eV according to the experimental procedure outlined earlier. Only three peaks were observed in this spectrum at m/e 28, m/e 19, and m/e 18 (Fig. 15). The peaks at m/e 28 and m/e 19 are attributable to N_2^+

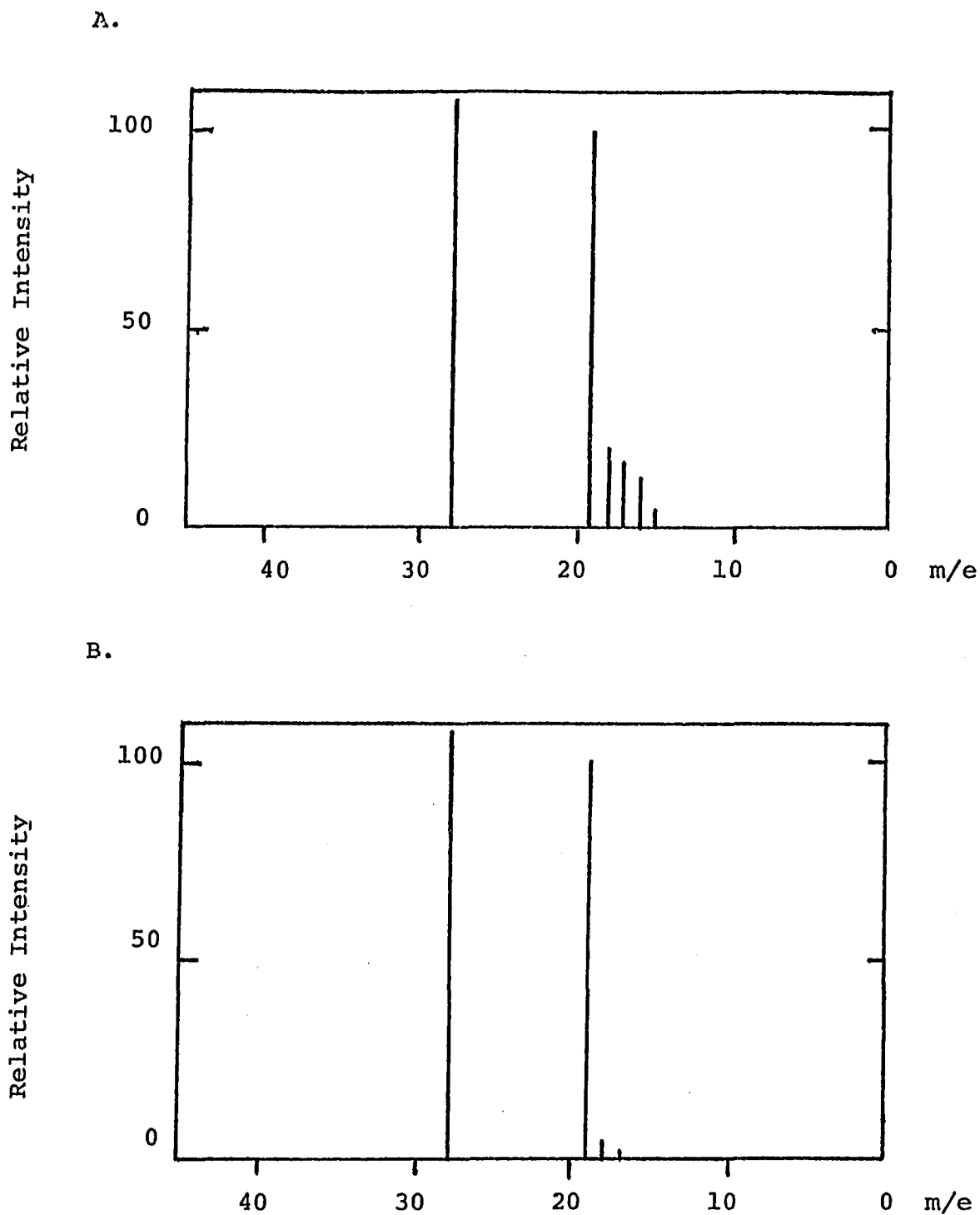


Fig. 15. Low Voltage Mass Spectra of the Liberated Methane during Photolysis of $(CD_3)_2Co(BDML,3pn)$, A., 20eV; B., 10eV.

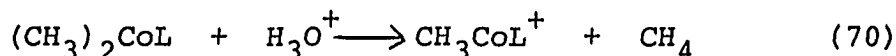
and CD_3H^+ respectively. The small peak at m/e 18 was assigned to H_2O^+ and not CD_2H_2 since the spectrum of 2-propanol gave a peak at m/e 18 of identical intensity (Table III). Background H_2O was a common impurity throughout this experiment, and could not be totally eliminated even by pumping down the system to 10^{-7} Torr overnight. It appears then that CD_3H is the only alkane product formed, thus confirming the proposed homolytic process for the photodecomposition of $(\text{CH}_3)_2\text{CoL}$.

Solid State Photolysis. Crystalline $(\text{CH}_3)_2\text{CoL}$ is relatively stable to light in the presence of O_2 or N_2 . Samples were exposed to sunlight for a period of several weeks and the organic products monitored by GLC. After approximately 3 weeks some discoloration of the solid was noted, however only traces of CH_4 and C_2H_6 were detected. Methane was the major product in both reactions and represented 99+% of the total organic products formed. These results are explained by the formation of a methyl radical followed by its abstraction of a hydrogen atom from the ligand (29). The presence of trace amounts of C_2H_6 , however, suggests that the dimerization of two methyl radicals is a competing reaction.

Reaction with H_3O^+

Stoichiometry and Products. In contrast to the monoalkylcobalt chelates which are not dealkylated by H_3O^+ (15,16), $(\text{CH}_3)_2\text{CoL}$ readily reacts with H_3O^+ in 2-propanol. Costa and co-workers (42,69) first reported the reaction of $(\text{CH}_3)_2\text{CoL}$ with H_3O^+ in aqueous-THF. The products CH_4 and CH_3CoL^+ were identified, but no information regarding the stoichiometry or rate of this reaction was reported. Consequently, a detailed study was initiated to obtain this information.

The stoichiometry of this reaction was determined by spectral titration using a standardized HClO_4 solution in 2-propanol. A plot of absorbance versus mole ratio ($\text{complex}/\text{H}_3\text{O}^+$) gave an end point at a molar ratio = 1.0 (Fig. 16), thus confirming the 1:1 stoichiometry of the reaction (Eqn. 70). The rate of methane



evolution (determined by GLC) was essentially instantaneous upon reacting $(\text{CH}_3)_2\text{CoL}$ with an equimolar amount of H_3O^+ .

Kinetics. Kinetic studies on the reactions of $(\text{CH}_3)_2\text{CoL}$ with excess H_3O^+ in 2-propanol show a first-

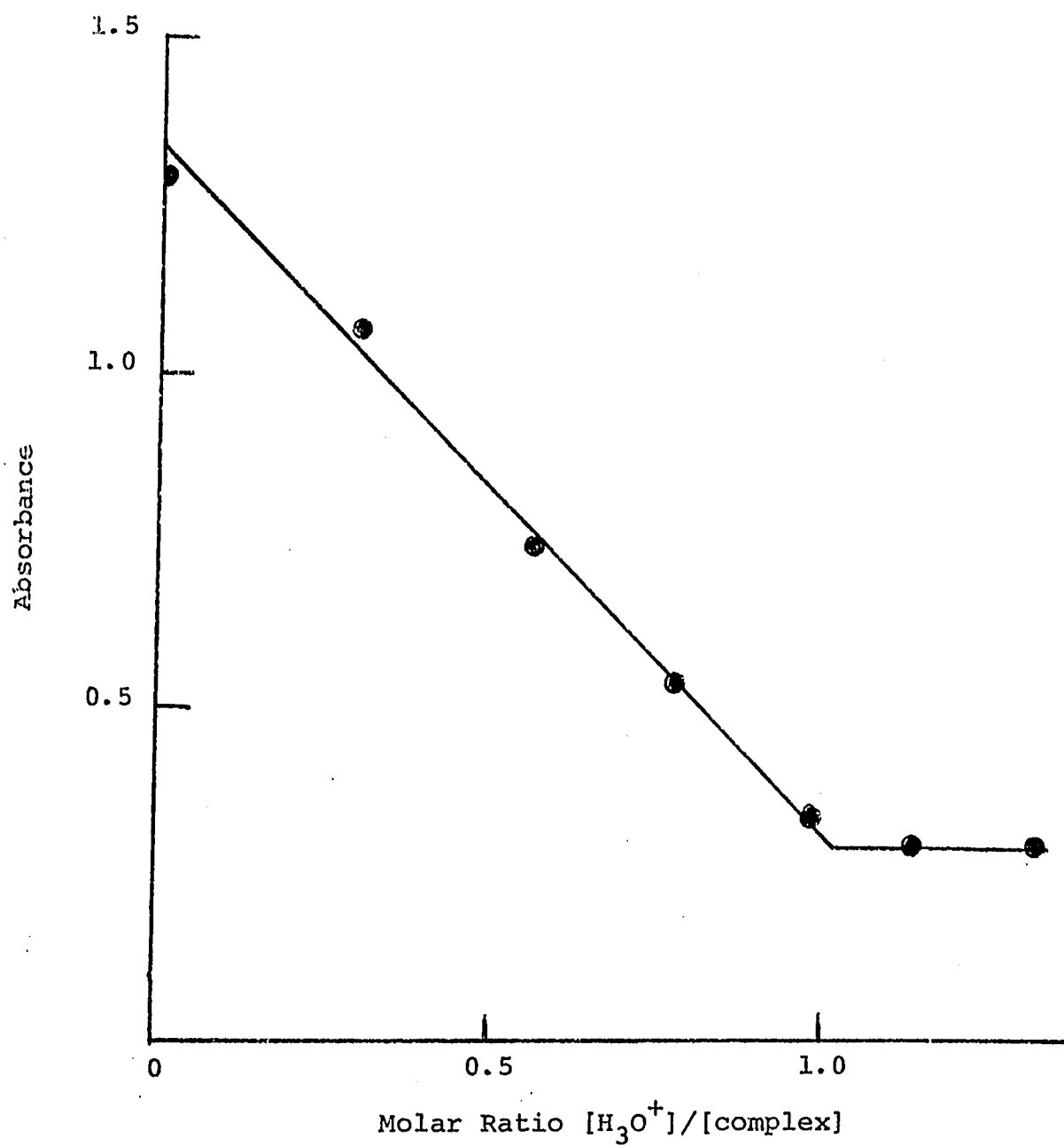


Fig. 16. Representative Spectral Titration of $(CH_3)_2Co(BDML,3pn)$ with H_3O^+

order dependence on the concentration of the dimethyl complex as depicted for typical reactions in Figure 17. The values of k_{obs} were determined from the slopes of these lines and are linear in $[\text{H}_3\text{O}^+]$ as shown in Figure 18.

Each of these reactions follows a second-order rate expression (Eqn. 71) with second-order rate con-

$$\frac{-d(\text{CH}_3)_2\text{CoL}}{dt} = k[(\text{CH}_3)_2\text{CoL}][\text{H}_3\text{O}^+] \quad (71)$$

stants of $104.4 \text{ M}^{-1} \text{ sec}^{-1}$ and $79.8 \text{ M}^{-1} \text{ sec}^{-1}$ for ionic strengths of $\mu = 0.05\text{M}$ and $\mu = 0.10\text{M}$ respectively.

These results support a $\text{S}_{\text{E}}2$ mechanism in which there is a direct transfer of the methyl group to H_3O^+ in a transition state formed by the bimolecular interaction of the two reactants. The small medium effect seen here was unexpected since $(\text{CH}_3)_2\text{CoL}$ is a neutral complex. Presumably, the slower rate observed at $\mu = 0.10\text{M}$ reflects a decrease in the activity of H_3O^+ at the higher ionic strength.

It is of interest to compare the results observed here with those obtained by Espenson et al. for the reactions of H_3O^+ with $[(\text{CH}_3)_2\text{Co}(\text{tim})]^+$ (40). In agreement with our data a second-order rate expression was followed indicating a similar mechanism for the two reactions. However, the second-order rate constant

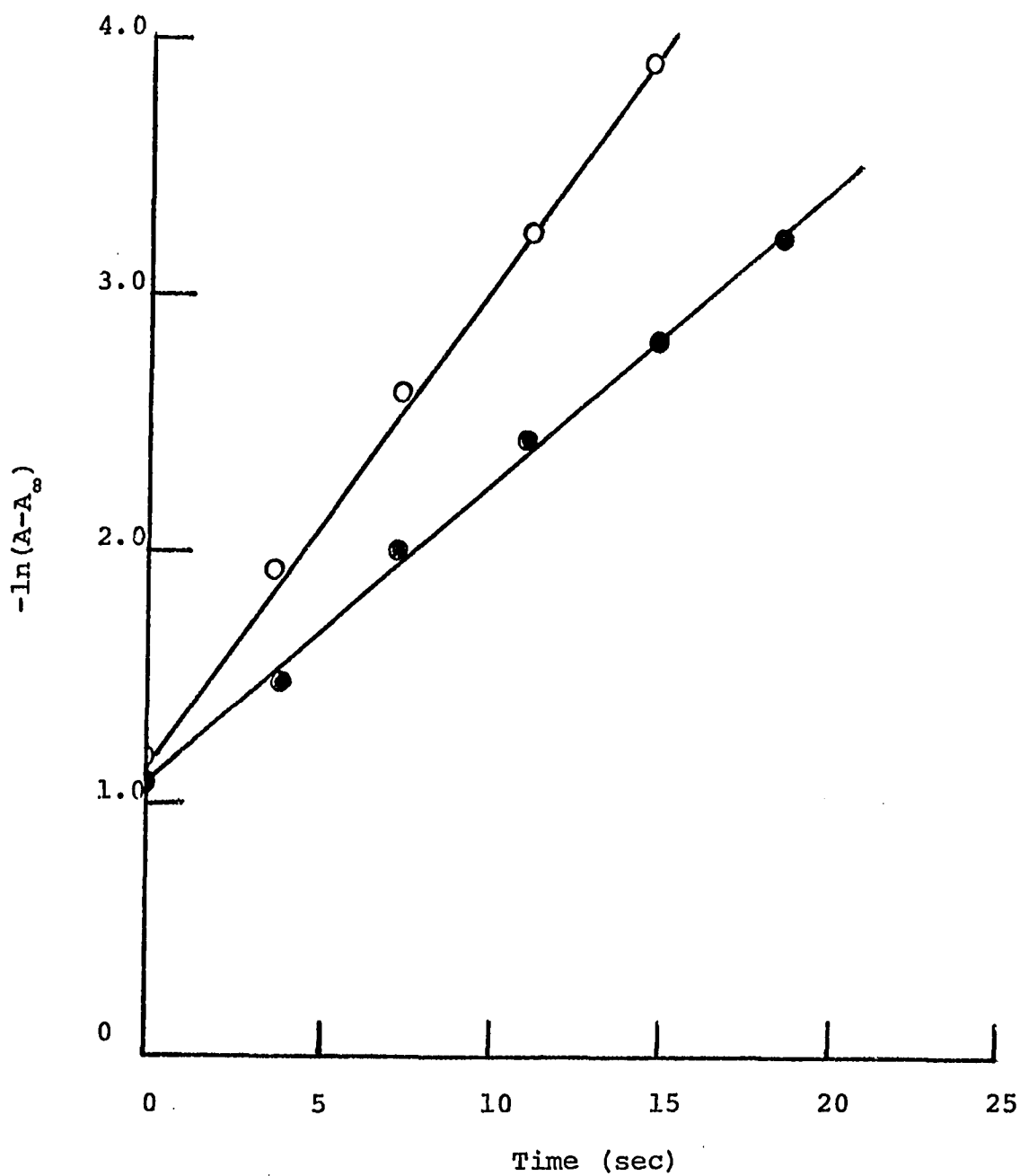


Fig. 17. Representative Plots of $\ln(A-A_\infty)$ versus Time for the Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ with H_3O^+ ; $1.15 \times 10^{-3}\text{M}$ ●; $1.43 \times 10^{-3}\text{M}$, ○; $\mu = 0.1\text{M}$.

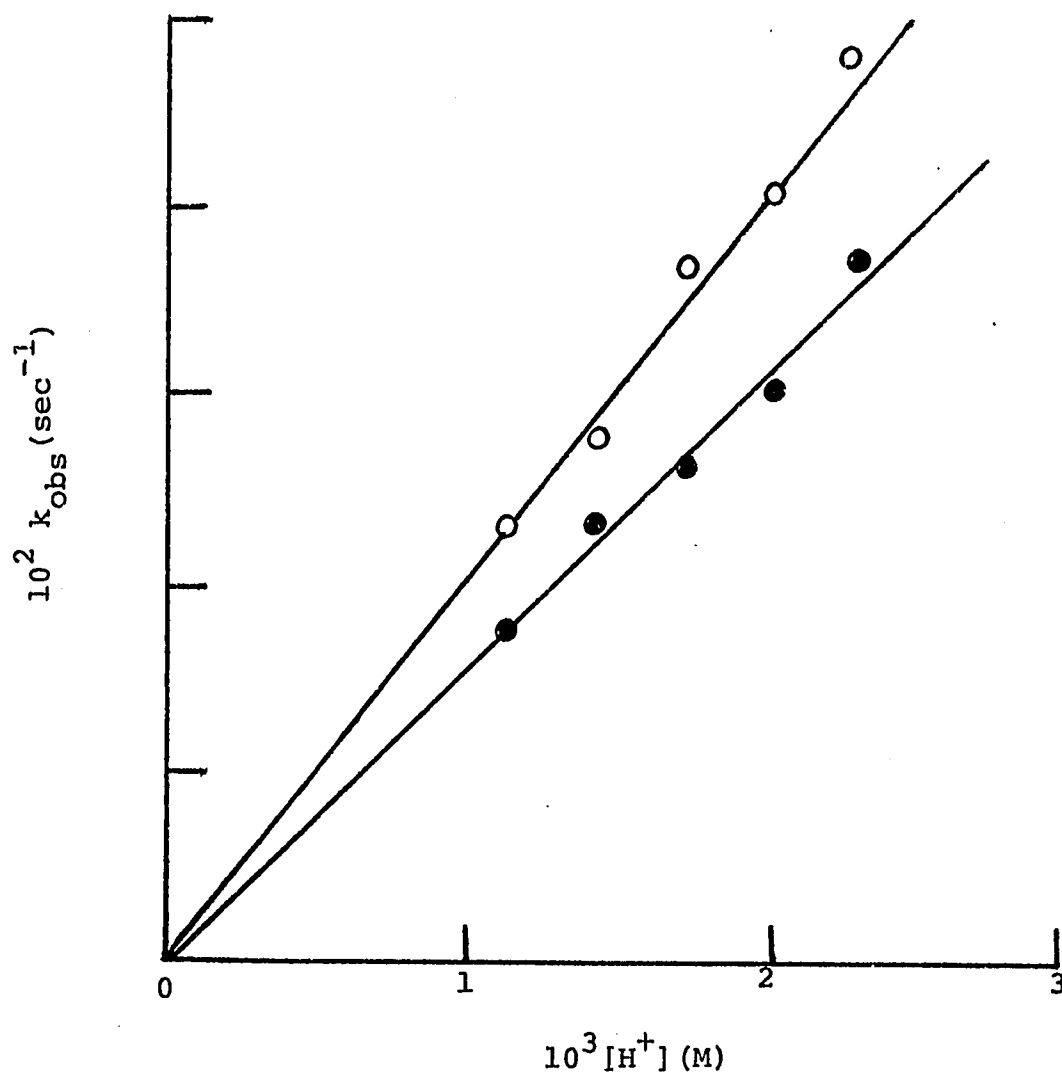
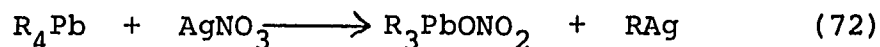


Fig. 18. Variation of k_{obs} with $[\text{H}_3\text{O}^+]$;
 $\mu = 0.05, \text{O}$; $\mu = 0.10, \bullet$.

is lower by a factor of about 300. The slower rate of reaction observed for the positively charged $[(CH_3)_2Co-(tim)]^+$ complex relative to the neutral $(CH_3)_2CoL$ complex presumably reflects the expected electrostatic repulsion between the two positively charged reactants. However, the different solvent system used (1:1 THF- H_2O) may also be a contributing factor.

Reaction with Ag^+

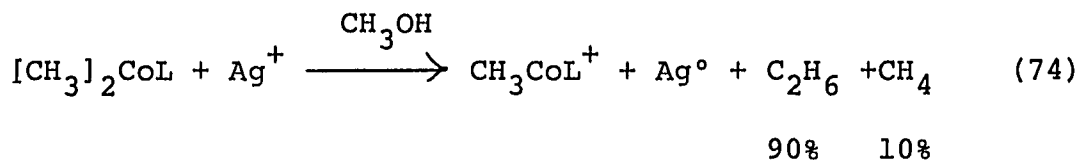
Silver nitrate reacts with a variety of tetra-alkyllead compounds in alcoholic solutions to yield metastable σ -bonded alkyl silver(I) compounds of the type RAg ($R = CH_3, C_2H_5, C_3H_7$ etc.) (106) (Eqn. 72). These



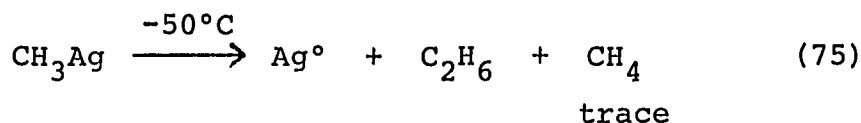
yellow to red-brown compounds decompose slowly at $-80^\circ C$ to yield metallic silver and a variety of gaseous hydrocarbons (Eqn. 73).



In analogy to the above reactions $(CH_3)_2CoL$ reacts instantaneously with a methanolic solution of $AgNO_3$ at room temperature to yield a silver mirror, and ethane as the predominant organic product (Eqn. 74). When the

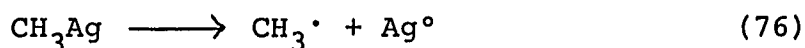


reaction was run at -78°C a yellow-brown precipitate slowly formed. This compound was attributed to CH_3Ag or $2\text{CH}_3\text{Ag}^\circ$ AgNO_3 (107), since the isolated material (separated by centrifugation) decomposed according to equation 75 upon warming to -50°C . This corresponds to the decomposition temp-



erature of CH_3Ag and other alkylsilver compounds (108).

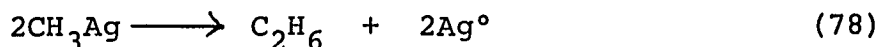
Little is known concerning the mechanism of hydrocarbon formation during the thermal decomposition of alkylsilver compounds. Previous investigators proposed a free radical mechanism (Eqns. 76 and 77) to account for the formation of ethane in the thermal decomposition of CH_3Ag (107,



109). A similar reaction scheme was proposed to account for the ethane, ethylene, and η -butane products observed for the thermolysis of $\text{C}_2\text{H}_5\text{Ag}$ (110). However, this was disputed by

by Kochi and Clinton (111) since the amount of butane formed was not influenced by the presence of radical scavengers such as O_2 .

To clarify the mechanism of C_2H_6 formation, the reaction of $(CH_3)_2CoL$ with Ag^+ was studied in several solvents. The results indicate that simple dimerization of free methyl radicals to yield C_2H_6 is not a major pathway. If this were the case, one would predict the formation of increasing amounts of CH_4 with the increasing ease of α -hydrogen abstraction from the solvent. Reactions run in H_2O , CH_3OH , C_2H_5OH and $i-C_3H_7OH$ did not demonstrate this effect since a constant amount of methane was obtained in all four solvents (Eqn. 74). These results are in agreement with the work of Kochi and Clinton (111) and suggest that no transient $CH_3\cdot$ intermediate exists in solution. The most reasonable explanation, as suggested for C_2H_5Ag , is a reaction between two molecules of CH_3Ag (Eqn. 78). The origin of methane is unknown at



this time but may arise from the protonolysis of either CH_3Ag or $(CH_3)_2CoL$; or both.

Reactions with Zn^{2+} , Cd^{2+} , and Pb^{2+}

In this section the reactions of $(\text{CH}_3)_2\text{CoL}$ with Zn^{2+} , Cd^{2+} , and Pb^{2+} in $i\text{-C}_3\text{H}_7\text{OH}$ will be discussed. These metal ions were previously shown to be unreactive toward a variety of organocobalt species (94,95). This study involves the elucidation of some very surprising reactions in which $(\text{CH}_3)_2\text{CoL}$ is unusually effective among methylcobalt complexes as a carbanion donor. In addition our data supports the formation of intermediate organometallic products of the type CH_3M^+ and $(\text{CH}_3)_2\text{M}$ which was entirely unexpected in view of the protic solvent employed.

In contrast to the reactions of the monoalkyl derivatives $\text{RCo}(\text{chel})$ with Hg^{2+} which demonstrate a simple 1:1 stoichiometry (Eqn. 79), the anaerobic reactions of



$(\text{CH}_3)_2\text{CoL}$ with Zn^{2+} , Cd^{2+} and Pb^{2+} are quite unique. Preliminary experiments revealed that two very different reactions occurred depending upon whether the metal ion or complex was in excess. In the presence of excess metal ion an instantaneous reaction was observed. With excess complex, however, the instantaneous reaction was followed by a slower reaction which was complete in a

matter of minutes. The biphasic nature of this reaction was confirmed using the stopped-flow technique. In order to facilitate the discussion, these two classes of reactions will be discussed separately beginning with the experiments using excess metal ion.

Reactions with excess Zn^{2+} , Cd^{2+} and Pb^{2+} . Upon reaction of $(\text{CH}_3)_2\text{CoL}$ with an equimolar or excess of Zn^{2+} , Cd^{2+} , or Pb^{2+} in $i\text{-C}_3\text{H}_7\text{OH}$ the ultraviolet-visible spectrum changes instantaneously. These reactions can be monitored most conveniently by observing the disappearance of the visible maximum at 412 nm ($\epsilon = 8380$) which is characteristic of $(\text{CH}_3)_2\text{CoL}$. The complex product ion CH_3CoL^+ was identified by comparison of the spectra of the final solutions with that of a solution made from an analyzed sample of $[\text{CH}_3\text{Co}(\text{L})\text{H}_2\text{O}]^+$. From a knowledge of the molar absorptivity of the product ion at 463 nm, ($\epsilon = 2120$) it is evident that $(\text{CH}_3)_2\text{CoL}$ is quantitatively converted to CH_3CoL^+ in these reactions. Furthermore, this monomethyl product is indefinitely stable in the presence of excess Zn^{2+} , Cd^{2+} , or Pb^{2+} in accord with the results of Magnuson (95) for the reactions of CH_3CoL^+ with the same metal ions in aqueous solution.

The stoichiometries of these fast reactions were determined by spectral titration (Fig. 19). This procedure was complicated by the overlapping of the second slower

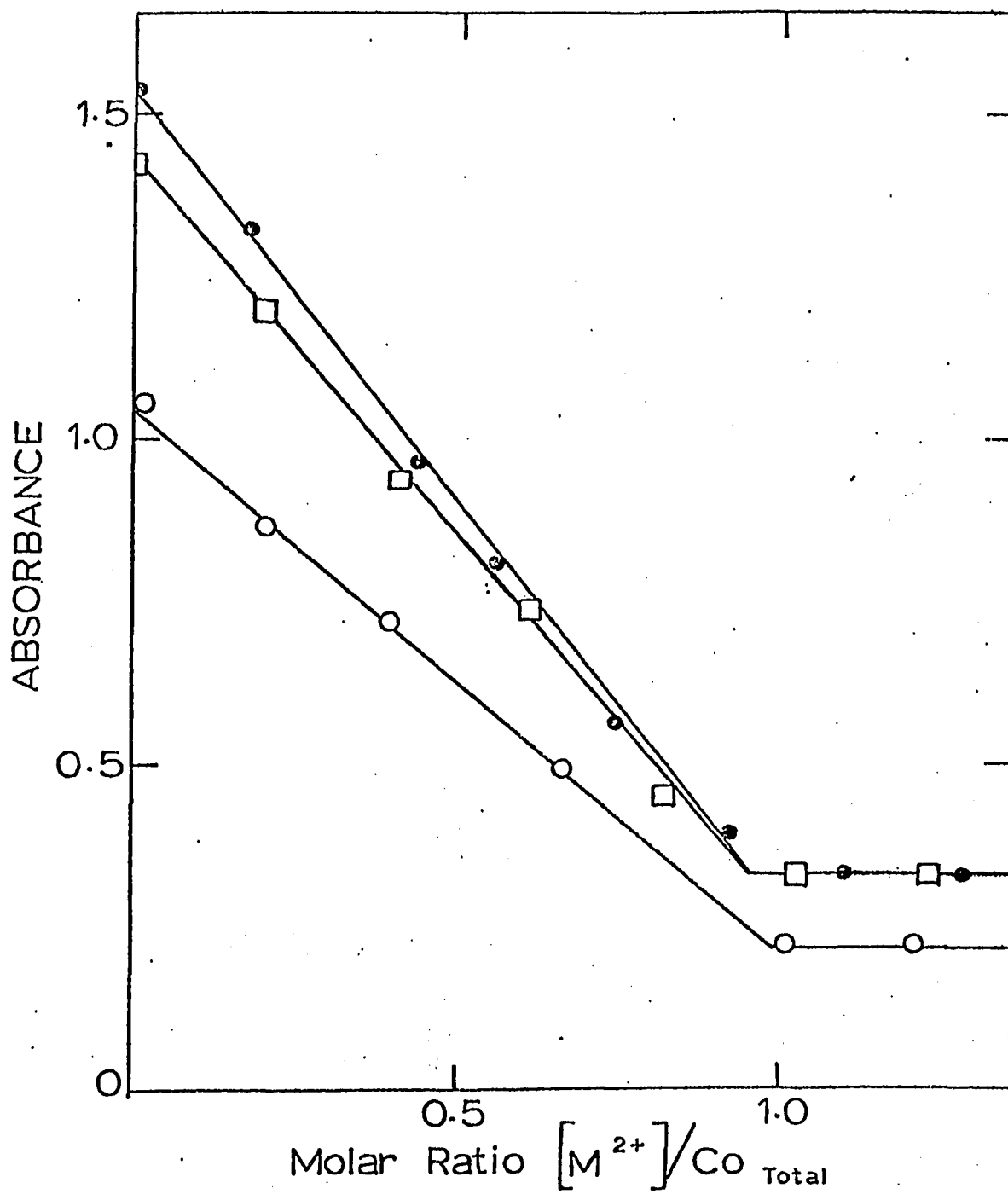
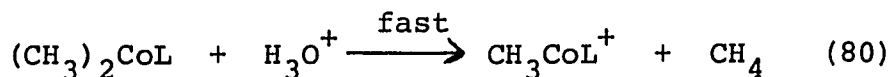


Fig. 19. Representative Spectral Titrations of the Fast Reaction between $(CH_3)_2Co(BDM1,3pn)$ and Zn^{2+} , ●; Cd^{2+} , □; and Pb^{2+} , ○.

phase of the reaction which was fairly rapid in the early stages. As a consequence a rapid titration technique was devised to minimize any error incurred due to the competing reaction (see EXPERIMENTAL). The method that was found to be most convenient was to deliver the M^{2+} titrant directly into a spectrophotometric cell, which contained an appropriate amount of complex, using a one microliter syringe. In this manner volume corrections were negligible and the titration could be carried out quite rapidly. The titrations for Zn^{2+} , Cd^{2+} and Pb^{2+} yield end points close to a molar ratio ($M^{2+}/\text{complex}$) equal to 1.0 (Fig. 19). The fact that the molar ratios are slightly low reflects the contribution due to the competing reaction.

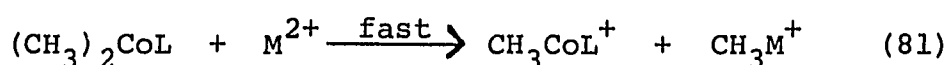
An interesting feature of this work is the fate of the liberated methyl group. The fast demethylation reactions described above are followed by relatively slow reactions in which methane is evolved. This is in contrast to the demethylation of $(CH_3)_2CoL$ by H_3O^+ in which the methane is liberated instantaneously and quantitatively according to (Eqn. 80). In fact, for the Cd^{2+} and



Pb^{2+} reactions the theoretical amount of methane was obtained only after ca. 200 hrs! The methane could be

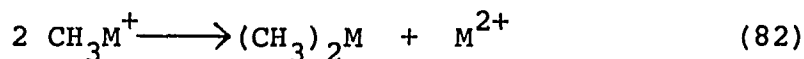
quantitatively recovered at any time during the course of the reaction, however, by the addition of H_3O^+ .

On the basis of the slow evolution of methane, the sensitivity of the intermediate species to H_3O^+ , and the indicated 1:1 stoichiometry, we postulate that intermediates of the type CH_3Zn^+ , $\text{CH}_3\text{Cd}^{2+}$, and CH_3Pb^+ are formed in these reactions according to equation 81. Further



support for these species comes from a study of the kinetics of their decomposition.

The rate of methane evolution was monitored by GLC for the reactions of $(\text{CH}_3)_2\text{CoL}$ with the three metal ions. Plots of $\ln(\text{C}_\infty - \text{C})$ versus time were linear over at least four half-lives as shown in Fig. 20. The rates were independent of excess metal ion concentration, which precludes the possibility of redistribution equilibria of the type shown in Eqn. 82. These results are



consistent with a process in which the organometallic intermediate is decomposed by $i\text{-C}_3\text{H}_7\text{OH}$ (Eqn. 83). Because



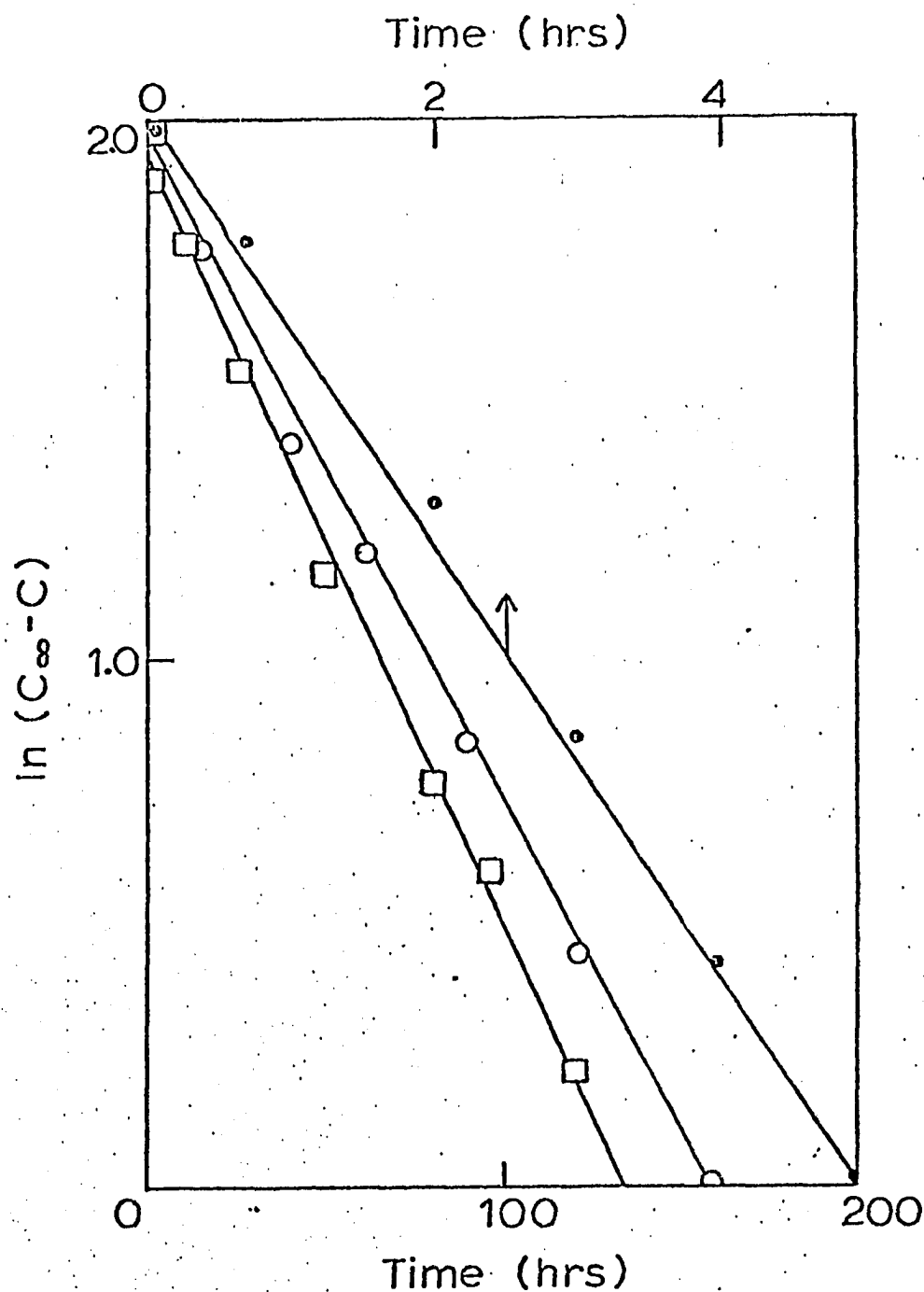


Fig. 20. Rate of Methane Evolution for the Reactions of $(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$ with Excess Zn^{2+} , \bullet ; Cd^{2+} , \square ; and Pb^{2+} , \circ .

the solvent is in a large excess over the CH_3M^+ species the reaction is pseudo-first order and the rate law (Eqn. 84) is followed.

$$\frac{d(\text{CH}_4)}{dt} = k_{\text{obs}}(\text{CH}_3\text{M}^+) \quad (84)$$

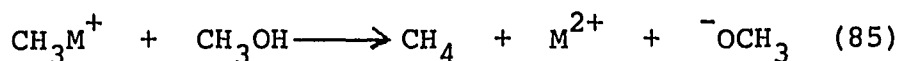
A summary of the kinetic data for the methane evolution reactions is presented in Table X. The relative stability $\text{CH}_3\text{Cd}^+ \gg \text{CH}_3\text{Zn}^+$ agrees with the known reactivity of saturated organometallic compounds of the Group IIB metals, $\text{Zn} > \text{Cd} > \text{Hg}$ (112). In addition the reactivity of organometallic compounds of the type RM^+ generally correlates with the ionic character of the carbon-metal bond; both decreasing in the order $\text{Li} > \text{Mg} > \text{Zn} > \text{Cd} > \text{Hg}$ (113). Consequently, the stability of CH_3Pb^+ observed here ($\text{CH}_3\text{Pb}^+ \sim \text{CH}_3\text{Cd}^+ > \text{CH}_3\text{Zn}^+$) agrees with the known covalent character of carbon-lead bonds (114).

Additional evidence for the formation of intermediates of the type CH_3M^+ comes from the accelerating effect of CH_3OH on the methane evolution reactions. The reactions of $(\text{CH}_3)_2\text{CoL}$ with excess Zn^{2+} , Cd^{2+} , and Pb^{2+} in solutions containing 20% (v/v) CH_3OH resulted in a considerably faster rate of CH_4 evolution. In fact, the reactions were complete in less than one hour. This is consistent with the protonolysis of CH_3M^+ by the more acidic CH_3OH (Eqn. 85). A similar reaction in which

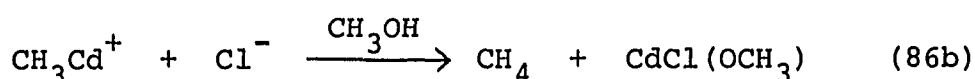
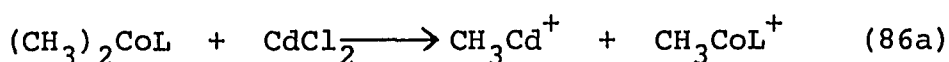
Table X. Summary of Kinetic Data for Methane Evolution during the Reactions of $(\text{CH}_3)_2\text{CoL}$ with Excess Zn^{2+} , Cd^{2+} , Pb^{2+} and H_3O^+ .

<u>Electrophile</u>	<u>$10^6 k_{\text{obs}} (\text{sec}^{-1})$</u>	<u>$t_{1/2} (\text{hrs})$</u>
Zn^{2+}	128	1.5
Cd^{2+}	3.6	52.6
Pb^{2+}	3.2	60.1
H_3O^+ ^a	--	--

^aThe theoretical amount of methane was obtained immediately after initiating the reaction.



$(\text{CH}_3)_2\text{CoL}$ was reacted with excess CdCl_2 in anhydrous methanol resulted in the rapid formation of a white precipitate together with the simultaneous evolution of CH_4 . This is consistent with a process (Eqn. 86) in which

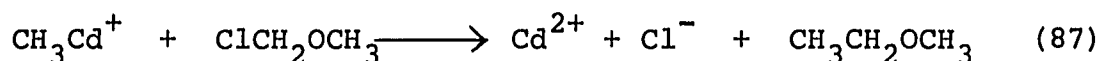


unstable CH_3Cd^+ formed in reaction (86a) reacts with CH_3OH in the presence of Cl^- to form solid $\text{CdCl}(\text{OCH}_3)$ (Eqn. 86b). This latter product was filtered from the reaction mixture, washed with CH_3OH , and identified by qualitative analysis and its strong absorption at 995 cm^{-1} due to $^-\text{OCH}_3$.

The apparent stability of the CH_3M^+ intermediates is somewhat surprising in view of the protic nature of the solvent. Solvation of the CH_3M^+ species by $i\text{-C}_3\text{H}_7\text{OH}$ presumably contributes to the stabilization of these organometallic intermediates, however, since oxygen donors are known to stabilize alkyl zinc and alkyl cadmium bonds (112). The isolation of stable alkyl zinc (115) and alkyl cadmium alkoxides (116) are good examples

of this effect.

Attempts to isolate the CH_3M^+ intermediates using stabilizing ligands such as Br^- , I^- , and bipy were unsuccessful. In addition, an attempt to trap CH_3Cd^+ by taking advantage of its expected reaction with chloromethyl ether (Eqn. 87) also failed. This was unexpected since

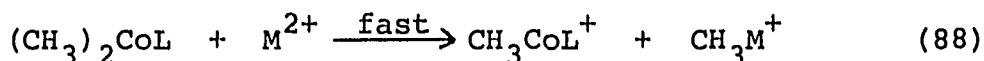


CH_3CdCl readily reacts with $\text{ClCH}_2\text{OCH}_3$ according to reaction (87) in diethyl ether (117). Despite these failures, however, the demonstrated 1:1 stoichiometry, the methane evolution data, and other evidence (see next section) strongly suggests that CH_3M^+ species are indeed intermediates in these reactions.

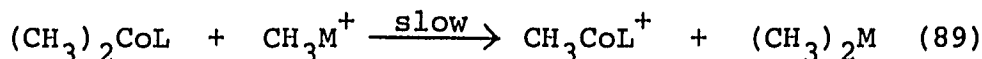
Reactions with excess $(\text{CH}_3)_2\text{CoL}$. The reactions of excess $(\text{CH}_3)_2\text{CoL}$ with Zn^{2+} , Cd^{2+} , and Pb^{2+} in $i\text{-C}_3\text{H}_7\text{OH}$ are markedly different from the reactions using excess metal ion. Instead of a single instantaneous reaction a two-step reaction was observed in which an initial fast step was followed by a relatively slow second reaction. The stoichiometries of these overall biphasic reactions were determined by spectral titration of $(\text{CH}_3)_2\text{CoL}$ with the standard solutions of the appropriate metal ion. The same technique as that employed for the titration of the fast reactions was utilized with the exception that the

reactions were allowed to proceed to completion. The results of these titrations for Zn^{2+} , Cd^{2+} , and Pb^{2+} are presented in Figures 21 and 22.

It is readily apparent that the end points for all three metal ions are close to a molar ratio ($\text{M}^{2+}/\text{complex}$) equal to 0.5; i.e. one mole of added metal ion reacts with two moles of $(\text{CH}_3)_2\text{CoL}$. This is consistent with a process in which the relatively stable CH_3M^+ intermediates formed in the initial fast reaction (Eqn. 88),



react with a second mole of $(\text{CH}_3)_2\text{CoL}$ in a subsequent slower reaction (Eqn. 89). The low molar ratio observed



for the Zn^{2+} titration is in agreement with the faster (Table X) protonolysis of CH_3Zn^+ by $i\text{-C}_3\text{H}_7\text{OH}$ (Eqn. 83). Thus, the reaction is catalytic in the sense that Zn^{2+} is continuously regenerated and reacts further with $(\text{CH}_3)_2\text{CoL}$ (Eqn. 88).

Support for the scheme outlined here comes from recent experiments conducted by Espenson et al. (40) on the methyl-transfer reactions of $(\text{CH}_3)_2\text{CoL}$, $[(\text{CH}_3)_2\text{Co}(\text{tim})]^+$, and $[(\text{CH}_3)_2\text{Co}(\text{CR})]^+$ with the analogous CH_3Hg^+

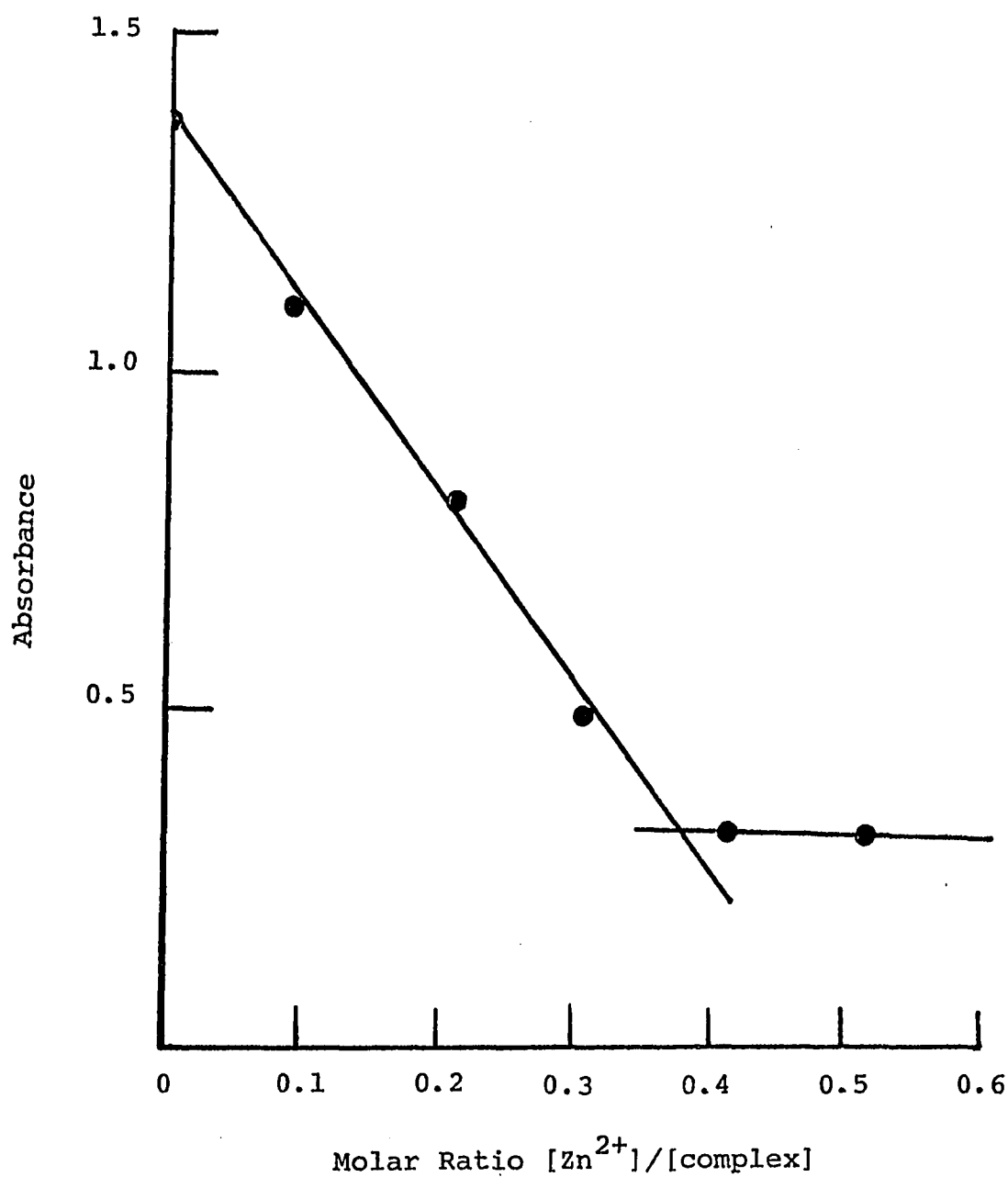


Fig. 21. Representative Spectral Titration for the Overall Biphaseic Reaction between $(\text{CH}_3)_2\text{Co}(\text{BDM1,3pn})$ and Zn^{2+}

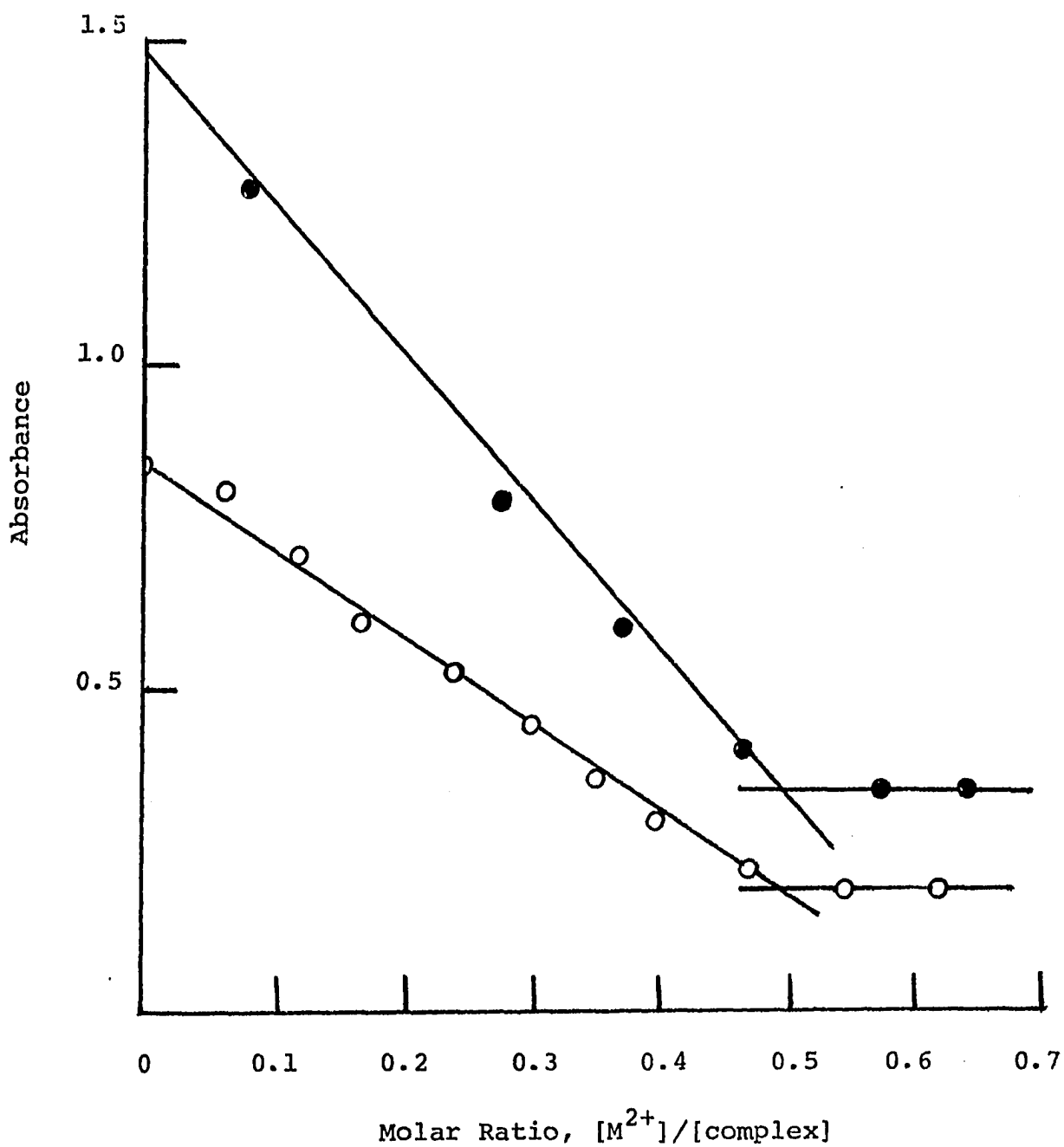
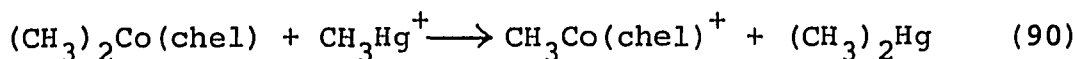


Fig. 22. Representative Spectral Titrations for the Overall Biphaseic Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDM}1,3\text{pn})$ with Cd^{2+} , O; and Pb^{2+} , ●.

species (Eqn. 90). These reactions occur with the indicat-



chel = BDML, 3pn, tim, CR

ed 1:1 stoichiometry and proceed to completion. Reaction (90) occurs also with $\text{C}_6\text{H}_5\text{Hg}^+$ (and probably with any other mono-organomercury derivative) as the acceptor, and with $(\text{C}_6\text{H}_5)_2\text{CoL}$, $(\text{C}_7\text{H}_7)_2\text{CoL}$, $[(\text{C}_2\text{H}_5)_2\text{Co}(\text{CR})]^+$, and $[(\eta\text{-C}_3\text{H}_7)_2\text{Co}(\text{CR})]^+$ as alkyl donor complexes.

The proposed dimethylzinc, dimethylcadmium and dimethyllead products (Eqn. 89) are extremely reactive, and are readily decomposed by compounds (including alcohols) which contain an active hydrogen (112,114). As a consequence, the rapid formation of methane was anticipated in these reactions. In fact, this was observed upon reacting $(\text{CH}_3)_2\text{CoL}$ with Cd^{2+} or Pb^{2+} in a molar ratio ($\text{M}^{2+}/\text{complex}$) equal to 0.5. This observation further corroborates the reaction scheme.

The reaction of $(\text{CH}_3)_2\text{CoL}$ with Cd^{2+} under these conditions results in the methane evolution profile shown in Figure 23. Two distinct steps are observed. In the first step 50% of the theoretical amount of methane (determined by the acid hydrolysis of $(\text{CH}_3)_2\text{CoL}$) is evolved in a matter of minutes. This is followed by a slow second step which liberates the remaining methane over a period of 150 hours. The methane evolution pattern

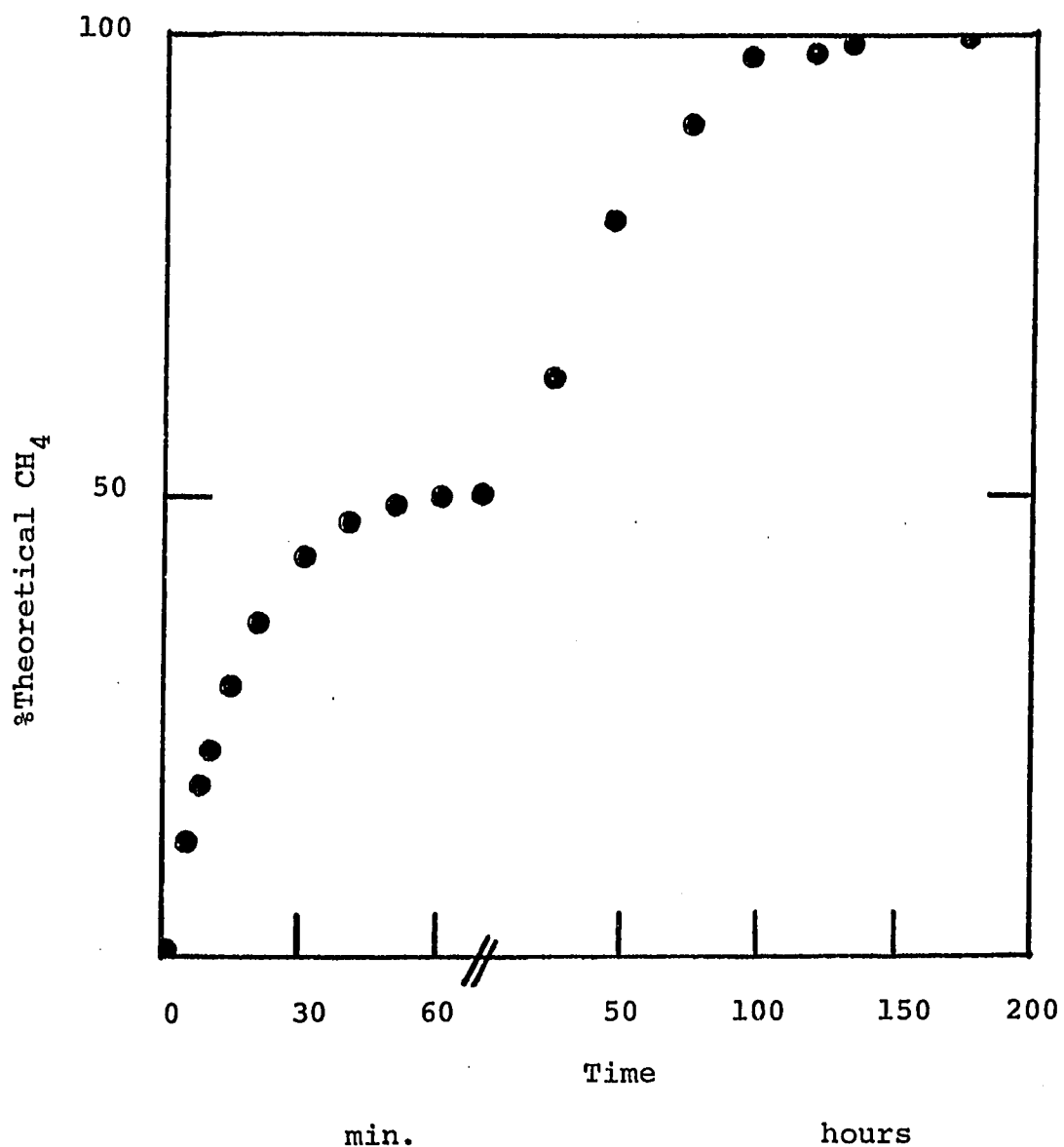
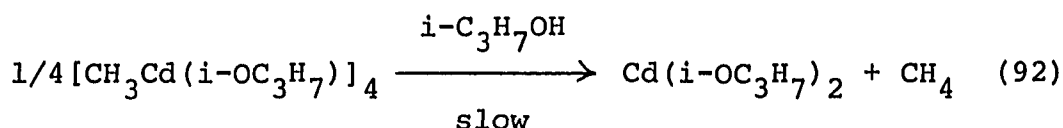
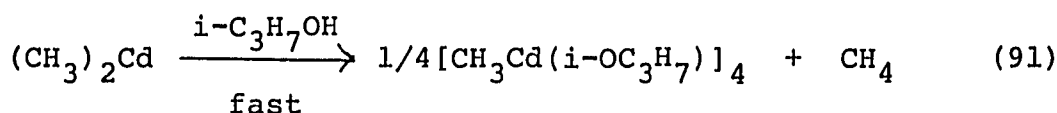


Fig. 23 Rate of Methane Evolution for the Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML}, 3\text{pn})$ with Cd^{2+} ($[\text{Cd}^{2+}]/[\text{complex}] = 0.5$).

seen here is consistent with a process in which the $(\text{CH}_3)_2\text{Cd}$ product formed in Eqn. 89, immediately reacts with $i\text{-C}_3\text{H}_7\text{OH}$ to form the well-known tetramer $[\text{CH}_3\text{Cd}(i\text{-OC}_3\text{H}_7)]_4$ (116), and CH_4 (Eqn. 91). The more stable tetramer is then slowly decomposed by $i\text{-C}_3\text{H}_7\text{OH}$ to liberate the remaining methyl group (Eqn. 92). This interpretation



is in agreement with recent kinetic and NMR studies of the reactions of $(\text{CH}_3)_2\text{Cd}$ and $(\text{C}_2\text{H}_5)_2\text{Cd}$ with a variety of alcohols ROH which show that the $[\text{CH}_3\text{Cd}(\text{OR})]_4$ products are formed much more rapidly than the $\text{Cd}(\text{OR})_2$ products (118).

Additional evidence for the proposed reaction scheme is provided in Figure 24. In this experiment $(\text{CH}_3)_2\text{CoL}$ was titrated with a standardized Cd^{2+} solution in the usual manner while simultaneously monitoring the quantity of methane evolved. The amount of methane liberated after each addition of titrant was determined by GLC, and compared to the theoretical value which was measured by the acid hydrolysis of $(\text{CH}_3)_2\text{CoL}$. Figure 24 clearly shows the expected 2:1 (complex: Cd^{2+}) stoichiometry

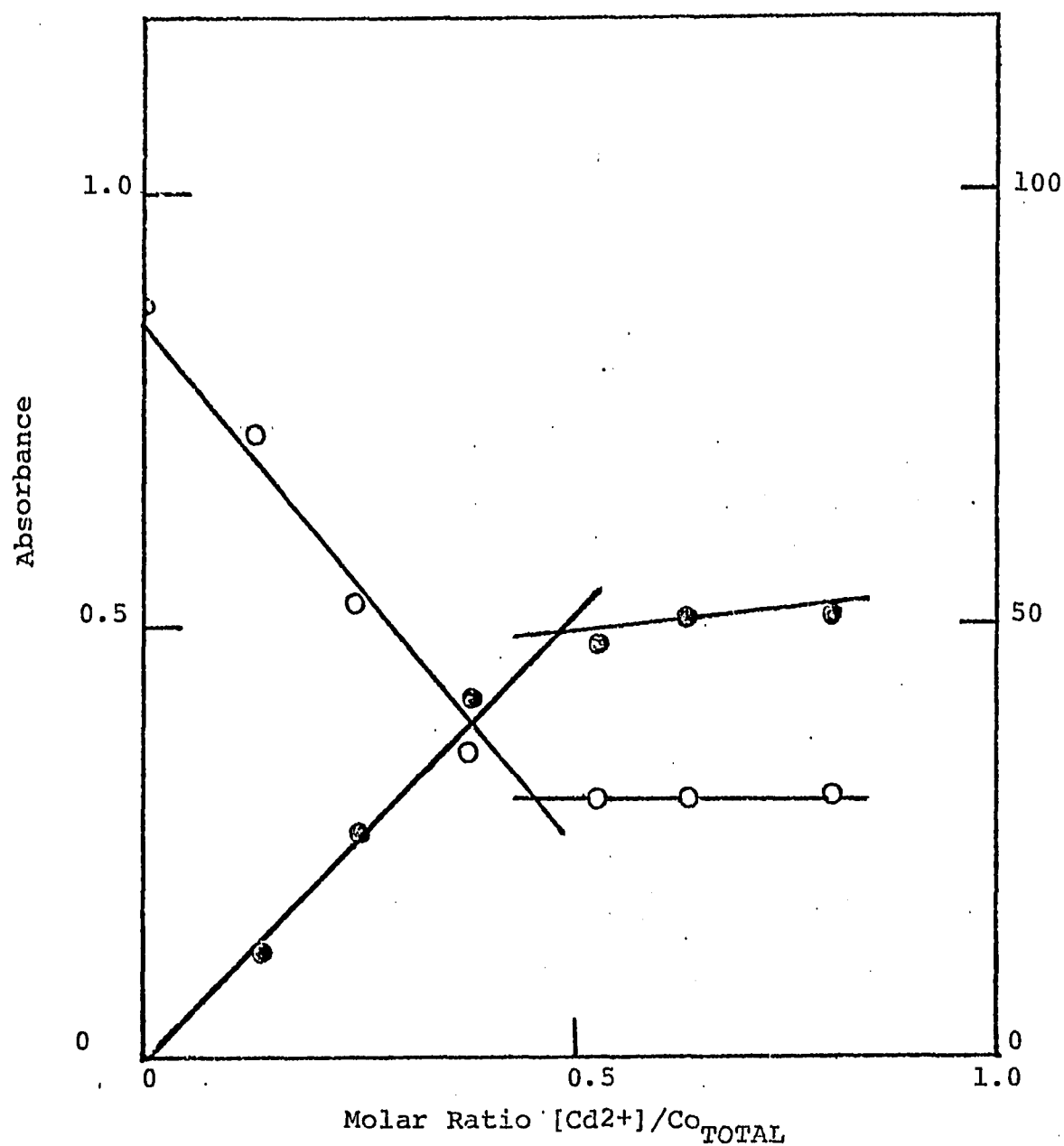
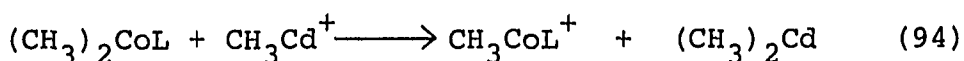
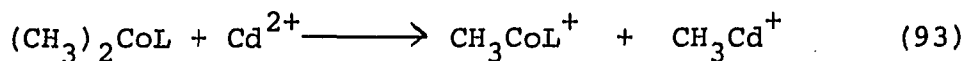


Fig. 24. Simultaneous Spectral Titration and Methane Evolution for the Reaction of $(CH_3)_2Co(BDML,3pn)$ with Cd^{2+} ($[Cd^{2+}]/[complex] = 0.5$); Titration O; CH_4 Evolution, ●.

(Eqns. 93 and 94). In addition it is evident that only

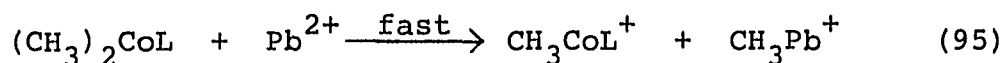


50% of the expected amount of methane is liberated upon reaching the end point, thus proving the transient existence of $(\text{CH}_3)_2\text{Cd}$.

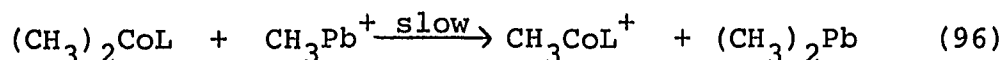
Perhaps the best evidence for the reaction scheme proposed here comes from the isolation of the well-known tetramer $[\text{CH}_3\text{Cd}(\text{i-OC}_3\text{H}_7)]_4$ as a product of the reaction of excess $(\text{CH}_3)_2\text{CoL}$ with Cd^{2+} (Eqns. 93 and 94). The reactions were run using a molar ratio $[\text{Cd}^{2+}]/\text{complex} = 0.5$ in 2-propanol. The white isopropoxide was recovered in low yield by freeze-drying the reaction mixture and subliming (10^{-3} Torr, 115°C) the residue. The tetramer was characterized by its reaction with 1M HClO_4 to yield CH_4 and by comparing its mass spectrum to that of an authentic sample prepared from the reaction of $\text{i-C}_3\text{H}_7\text{OH}$ with $(\text{CH}_3)_2\text{Cd}$. The molecular ion peak at m/e 744 confirms the polymeric nature of this compound.

The reaction of $(\text{CH}_3)_2\text{CoL}$ with Pb^{2+} is analogous to the reaction with Cd^{2+} in certain respects. The titration data (Fig. 22) is again consistent with a process in which CH_3Pb^+ , formed in an initial fast reaction

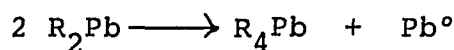
(Eqn. 95), reacts with a second mole of $(\text{CH}_3)_2\text{CoL}$ to



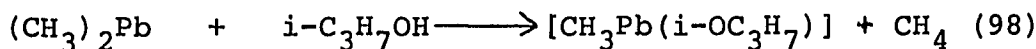
form $(\text{CH}_3)_2\text{Pb}$ (Eqn. 96). Divalent organolead compounds



are typically very unstable and frequently disproportionate into organolead(IV) species and lead metal (Eqn. 97) (114).



This reaction was not observed here, however. Instead, the reaction of $(\text{CH}_3)_2\text{CoL}$ with Pb^{2+} ($\text{Pb}^{2+}/\text{complex} = 0.5$) resulted in the methane evolution profile (Fig. 25), and the simultaneous formation of a light-brown precipitate. The fact that only 50% of the expected methane is ultimately observed suggests that the precipitate is a stable $[\text{CH}_3\text{Pb}(\text{i-OC}_3\text{H}_7)]$ compound formed by the protonolysis of $(\text{CH}_3)_2\text{Pb}$ (Eqn. 98). Presumably, the $[\text{CH}_3\text{Pb}(\text{i-OC}_3\text{H}_7)]$



product is polymeric in analogy to $[\text{CH}_3\text{Cd}(\text{i-OC}_3\text{H}_7)]_4$ since lead alkoxides reportedly exist as polymeric chains linked

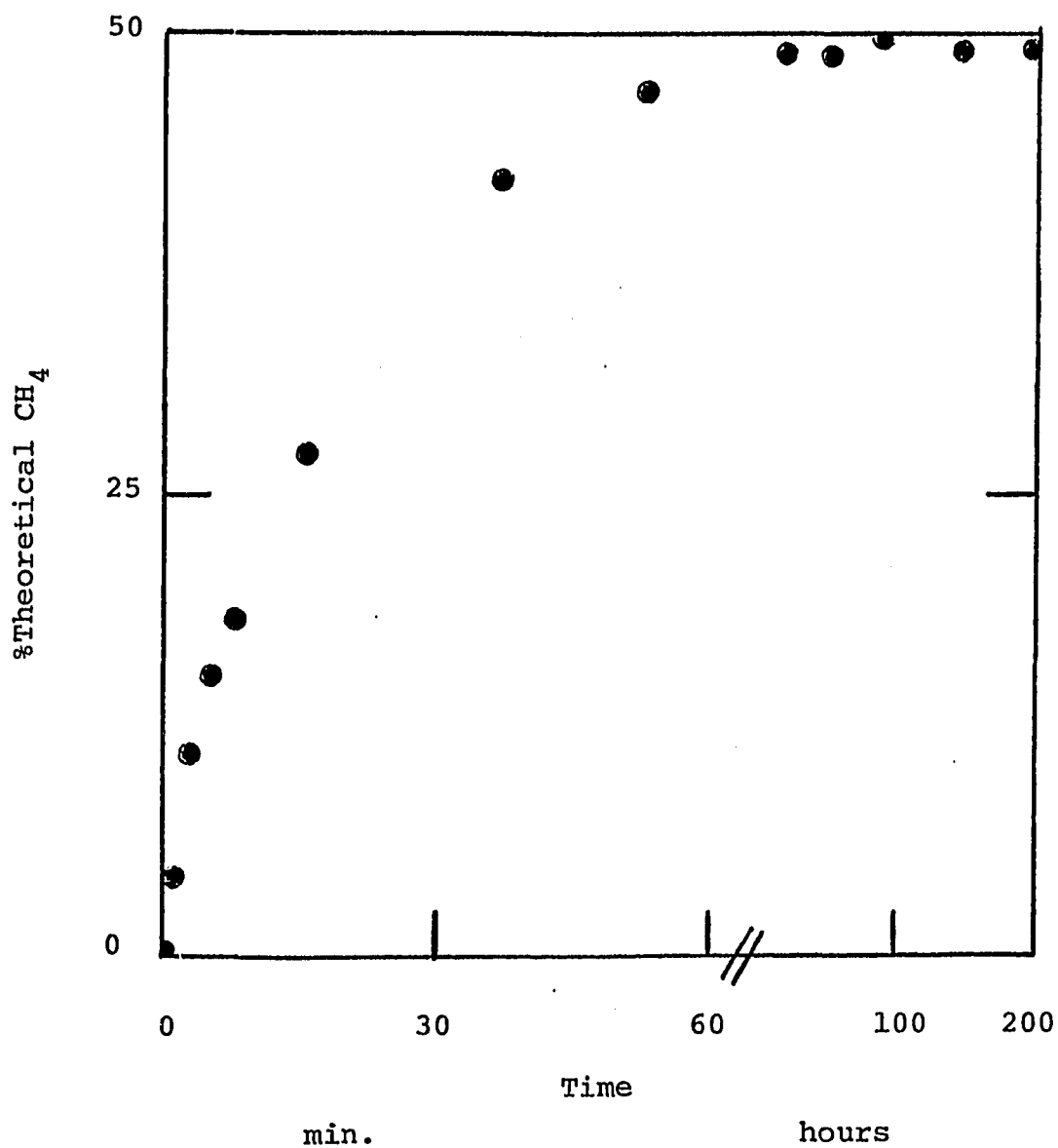
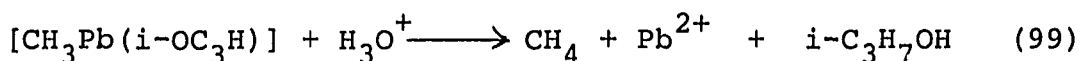


Fig. 25. Rate of Methane Evolution for the Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with Pb^{2+} ($[\text{Pb}^{2+}]/[\text{complex}] = 0.5$).

by oxygen atoms (119). The addition of H_3O^+ to the solution results in formation of the remaining methane and dissolution of the precipitate (Eqn. 99), thus lending



further support to this interpretation. Unfortunately, elemental analysis of the isolated precipitate did not confirm the presence of $[\text{CH}_3\text{Pb}(\text{i-OC}_3\text{H}_7)]$. The analysis indicated that N was present which suggested that the product was contaminated with CH_3CoL^+ . This was confirmed by dissolving the precipitate in H_2O or H_3O^+ and comparing the spectrum of the resulting orange colored solution to that of CH_3CoL^+ . Cold washing with 2-propanol did not improve the results indicating that CH_3CoL^+ is tightly held. The fact that analogous precipitates were not observed in the reactions of $(\text{CH}_3)_2\text{CoL}$ with excess Pb^{2+} , or upon mixing solutions of CH_3CoL^+ and Pb^{2+} precludes the presence of Pb^{2+} adducts as have been isolated from the reactions of Hg^{2+} with $\text{RCo}(\text{salen})$ complexes (68). Despite these negative results, however, the formation of CH_4 and $\text{i-C}_3\text{H}_7\text{OH}$ upon dissolution of the precipitate in H_3O^+ suggests that $[\text{CH}_3\text{Pb}(\text{i-OC}_3\text{H}_7)]$ is at least a minor product of these reactions.

Kinetics of the Reaction of $(\text{CH}_3)_2\text{CoL}$ with Excess Zn^{2+} and Cd^{2+}

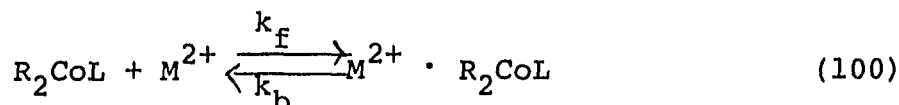
The kinetic behavior of the 1:1 reaction (Eqn. 81) of $(\text{CH}_3)_2\text{CoL}$ with Zn^{2+} and Cd^{2+} was investigated by monitoring the decrease in absorbance due to the complex at 412 nm. These reactions exhibited half-lives on the order of a few milliseconds, and were studied using the stopped-flow technique. The corresponding reaction with Pb^{2+} was not studied due to the unexplained extreme sensitivity of the reaction to oxygen, which resulted in the formation of brown precipitate.

Plots of the data (120) in the form $\ln(A-A_\infty)$ versus time were invariably linear over at least four half-lives for both metal ions. Since the metal ions were in excess over the complex, the observed kinetics were pseudo-first-order. A least squares analysis of the slopes of these lines yielded values for the observed rate constants (k_{obs}) which ranged from 85 to 180 sec^{-1} for Zn^{2+} , and 108 to 231 sec^{-1} for Cd^{2+} . The metal ion dependence of the reactions was determined by varying $[\text{Zn}^{2+}]$ and $[\text{Cd}^{2+}]$ from 7.25×10^{-5} to 2.25×10^{-4} M while maintaining the ionic strength constant at 1.8×10^{-3} M. The apparent second-order rate constants decreased markedly with increasing metal ion concentration throughout the range studied as can be seen in Table XI.

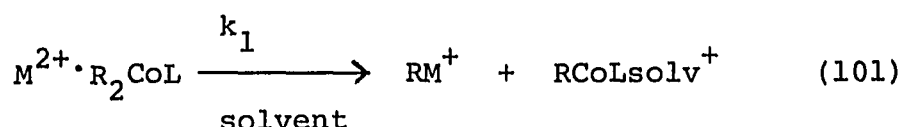
Table XI. Summary of Second-Order Rate Constants as a Function of Metal Ion Concentration

<u>Zinc (II)</u>		<u>Cadmium (II)</u>	
$10^5 [\text{Zn}^{2+}], (\text{M})$	$10^{-5} k_{\text{obs}} / [\text{Zn}^{2+}]$	$10^5 [\text{Cd}^{2+}], (\text{M})$	$10^{-5} k_{\text{obs}} / [\text{Cd}^{2+}]$
	$(\text{M}^{-1} \text{sec}^{-1})$		$(\text{M}^{-1} \text{sec}^{-1})$
7.25	11.7	3.75	28.7
10.7	10.7	5.62	25.3
12.9	10.1	7.50	22.6
16.5	9.2	15.0	15.4
22.5	8.0		

The most reasonable explanation of this phenomenon is that there is a rapid pre-equilibrium between the reactants and a substitutionally labile 1:1 adduct that is being saturated as the concentration of the metal ion is increased (Eqn. 100). This process is followed by the



rate determining decomposition of the adduct to products (Eqn. 101), where $R = CH_3$ in this scheme. If $K = k_f/k_b$



and $k_b \gg k_1$, the rate law (Eqn. 102) is derived. Plots

$$\frac{-d[R_2CoL]}{dt} = \frac{k_1 K [M^{2+}] [R_2CoL]}{1 + K [M^{2+}]} \quad (102)$$

of the reciprocal of the observed pseudo-first-order rate constant versus the reciprocal of the metal ion concentration are linear in agreement with this scheme. The data indicating this linear relationship are presented in Fig. 26. The kinetic and equilibrium parameters were extracted from the slopes and intercepts of these lines and are summarized in Table XII.

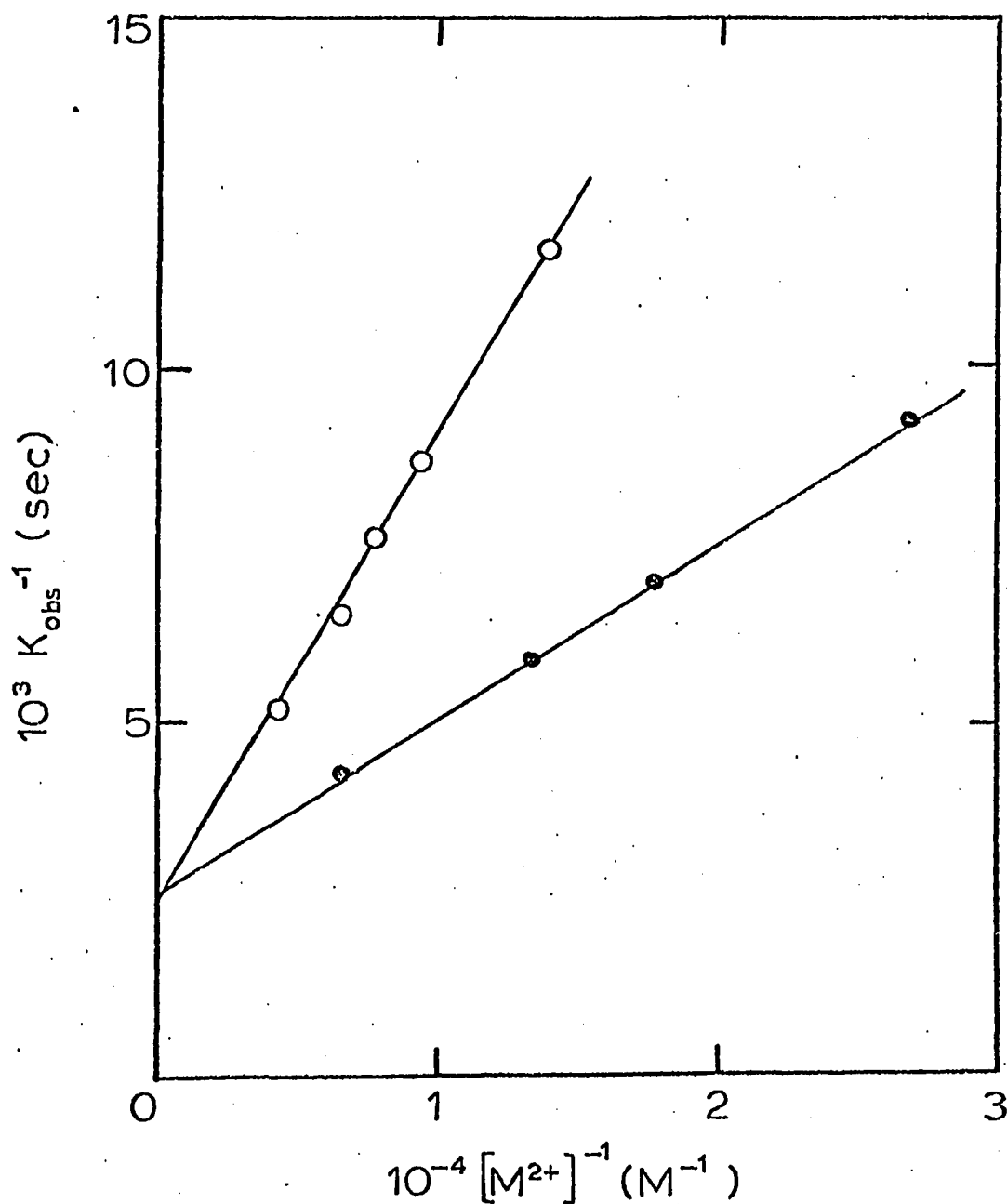


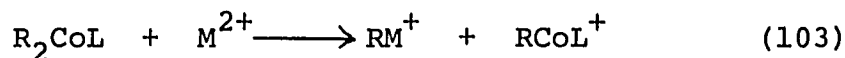
Fig. 26. Variation of k_{obs}^{-1} with $[M^{2+}]^{-1}$ for the Reactions of $(CH_3)_2Co(BDM1,3pn)$ with Excess Zn^{2+} , O; and Cd^{2+} , ●.

Table XII. Summary of Kinetic and Equilibrium Data^a for the Reaction of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with Zn^{2+} and Cd^{2+} .

Electrophile	$10^{-3}K(\text{M}^{-1})$	$10^{-2}k_1\text{sec}^{-1})$	$10^{-6}k_1K(\text{M}^{-1}\text{sec}^{-1})$
Zn^{2+}	3.8	3.8	1.4
Cd^{2+}	10.6	4.0	4.2

^aAt 22.2°C, $\mu = 1.8 \times 10^{-3}$ ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$) in $i\text{-C}_3\text{H}_7\text{OH}$.

The proposed first-order decomposition of the adduct (Eqn. 101) is not easily distinguished from a second-order reaction of metal ion with free R_2CoL (Eqn. 103) since both processes lead to the same kinetics.



However, we favor the former reaction (Eqn. 101) in view of the nearly identical k_1 values observed for both the Zn^{2+} and Cd^{2+} reactions. If the leaving group RM^+ is loosely held in the adduct similar k_1 values are expected. The slight difference in $k_1[Cd^{2+}] > k_1[Zn^{2+}]$ may reflect the size difference and thus the lability of the leaving group in the order $RCd^+ > RZn^+$. Presumably, adduct decomposition occurs by way of a five-coordinate intermediate since CH_3 is known to promote the dissociation of trans ligands in octahedral cobalt complexes (121). Furthermore, five-coordinate alkyl cobalt intermediates are well known in the anation reactions of $[RCo(L)H_2O]^+$ and alkylcobaloximes (122).

It is not surprising that adduct formation occurs in these reactions since 1:1 adducts were detected in the analogous reactions of the Group IIB metal ion Hg^{2+} with the monoalkylcobalt complexes $[RCo(L)H_2O]^+$ and $RCo(salen)$ (68); and with $ClCH_2Co(dmgl)_2H_2O$ (87). Adducts were not detected in the reactions of Hg^{2+} with other monoalkyl cobalt complexes. However, these reactions may be limiting

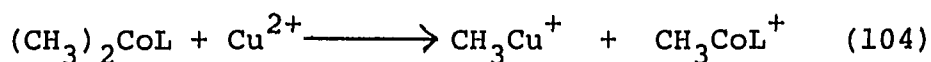
cases in which $K[\text{Hg}^{2+}] < 1$ and thus simple second-order kinetics were observed.

Finally, it is of interest to compare the Co-C bond reactivity of the trans-dimethyl complex $(\text{CH}_3)_2\text{CoL}$ observed here, with that of the corresponding monomethyl complex $[\text{CH}_3\text{Co}(\text{L})\text{H}_2\text{O}]^+$. The superior trans labilizing influence of CH_3 relative to H_2O is reflected in the large k_1K values for the reactions of $(\text{CH}_3)_2\text{CoL}$ with Cd^{2+} and Zn^{2+} . These same metal ions are unreactive toward $[\text{CH}_3\text{Co}(\text{L})\text{H}_2\text{O}]^+$ (95). In addition, the monomethyl complex is unreactive toward excess H_3O^+ while a second-order rate constant of $79.2 \pm 6.2 \text{ M}^{-1} \text{ sec}^{-1}$ was observed for $(\text{CH}_3)_2\text{CoL}$ in $i\text{-C}_3\text{H}_7\text{OH}$. These results are presumably a manifestation of the superior σ -donor capability of CH_3 , (123) which activates the trans methyl group for electrophilic attack by Zn^{2+} , Cd^{2+} , and H_3O^+ .

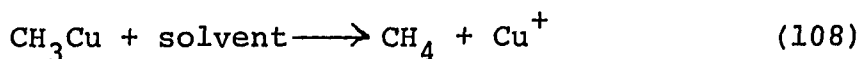
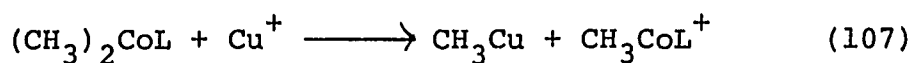
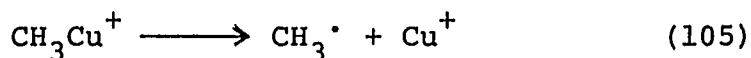
Reactions with Cu^{2+} and Cr^{3+}

The reactions of $(\text{CH}_3)_2\text{CoL}$ with these metal ions were studied as part of a preliminary screening process which was designed to identify the more interesting reactions for further study. Although these ions proved to be of potential interest in this regard, time did not allow the completion of an in-depth investigation of these reactions. Consequently, only preliminary results will be reported here in order to provide a starting point for further study.

The reaction between cupric ion and excess $(\text{CH}_3)_2\text{CoL}$ at room temperature in methanol follows a markedly different course from that of the silver ion reaction. In the latter case ethane was the major organic product, however, with Cu^{2+} the hydrocarbons formed contain large amounts of methane in addition to ethane. Presumably, a methylcopper(II) intermediate is formed in this reaction (Eqn. 104) in analogy to



the reaction of dimethylaluminum monoethoxide with Cu^{2+} (123). The ethane and methane products may be due to the homolysis of CH_3Cu^+ (Eqn. 105) followed by the reaction of Cu^{2+} with $(\text{CH}_3)_2\text{CoL}$ to yield CH_3Cu (Eqn. 107), which hydrolyses to give methane (Eqn. 108). Evidence for this scheme was presented earlier for the reaction of $(\text{CH}_3)_4\text{Pb}$ with Cu^{2+} (106).



The reaction of $(\text{CH}_3)_2\text{CoL}$ with $\text{CrCl}_3 \cdot 3\text{H}_2\text{O}$ resulted in a rapid reaction which liberated methane exclusively and formed CH_3CoL^+ . Presumably, $\text{CH}_3\text{Cr}^{2+}$ intermediates are involved as have been observed in the reactions of CH_3MgI with Cr^{3+} (124). The methane may well be formed by an α -elimination process since stable chromium-carbene complexes are well known (124). The use of $(\text{CD}_3)_2\text{CoL}$ should prove useful in the future investigation of these reactions.

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APPENDIX I

Kinetics Data for the Decomposition

 $(\text{CH}_3)_2\text{CoL}$ in Solution

The data reported here was collected for the protonolysis reactions of $(\text{CH}_3)_2\text{CoL}$ in H_2O , methanol, ethanol, and 2-propanol. The observed rate constants (k_{obs}) and the correlation coefficient (cc) are given at the end of each table. The k_{obs} values are identical to the regression coefficients obtained from the least squares fit of $\ln(A-A_\infty)$ versus time plots, and were obtained by using the STATPACK program provided by the computer center of the University of New Hampshire

Decomposition of $(\text{CH}_3)_2\text{CoL}$ in Solution

<u>H_2O</u>	<u>Time (min.)</u>	<u>$A-A_\infty$</u>	<u>$-\ln(A-A_\infty)$</u>
	0	0.300	1.20
	5	0.245	1.41
	10	0.210	1.56
	20	0.131	2.03
	25	0.108	2.23
	$k_{\text{obs}} (\text{min}^{-1})$	$= 4.15 \times 10^{-2}$	
	cc	$= 0.999$	
<u>CH_3OH</u>			
	0	0.310	1.17
	15	0.290	1.23
	28	0.259	1.35
	86	0.176	1.74
	134	0.115	2.16
	$k_{\text{obs}} (\text{min}^{-1})$	$= 7.39 \times 10^{-3}$	
	cc	$= 0.999$	

95% C₂H₅OH

<u>Time (min)</u>	<u>(A-A_∞)</u>	<u>-ln (A-A_∞)</u>
0	0.630	0.462
30	0.550	0.598
60	0.450	0.798
108	0.315	1.160
135	0.260	1.350
$k_{\text{obs}} (\text{min}^{-1})$	6.75×10^{-3}	
cc	0.998	

i-C₃H₇OH

<u>Time (hrs.)</u>	<u>(A-A_∞)</u>	<u>-ln (A-A_∞)</u>
0	0.883	0.124
10	0.860	0.151
22	0.837	0.178
95	0.677	0.390
125	0.565	0.571
166	0.520	0.654
$k_{\text{obs}} (\text{min}^{-1})$	5.52×10^{-5}	
cc	0.997	

APPENDIX II

Kinetics Data for Anaerobic Photolysis of $(\text{CH}_3)_2\text{CoL}$

The data reported here was collected for the anaerobic photolysis of $(\text{CH}_3)_2\text{CoL}$ in ethanol and 2-propanol.

A. Ethanol, $[(\text{CH}_3)_2\text{CoL}] = 10^{-4}\text{M}$

<u>Time (min.)</u>	<u>A-A_∞</u>	
	<u>1</u>	<u>2</u>
0	1.465	1.700
5.0	1.260	1.497
10.0	1.138	1.362
15.0	1.022	1.247
20.0	0.922	1.145
25.0	0.836	1.074
30.0	0.760	0.986
40.0	0.620	0.871
50.0	0.505	0.745
		0.019
$k_{\text{obs}} (\text{min}^{-1})$	0.021	0.019
cc	1.000	0.999

B. 2-propanol, $[(\text{CH}_3)_2\text{CoL}] = 10^{-4}\text{M}$

0	1.003	1.000
5.0	0.720	0.715
10.0	0.565	0.560
15.0	0.460	0.455
20.0	0.374	0.361
25.0	0.303	0.302
35.0	0.210	0.200
45.0	0.145	0.139
$k_{\text{obs}} (\text{min}^{-1})$	0.042	0.044
cc	1.000	0.999

APPENDIX III

Kinetic Data for the Reaction
of $(\text{CH}_3)_2\text{CoL}$ with $[\text{H}_3\text{O}^+]$.

A. $\mu = 0.1M$, $[(CH_3)_2CoL] = 10^{-4}M$

$$[H_3O^+] = 1.15 \times 10^{-3}M$$

<u>Time (sec)</u>	<u>A-A_∞</u>	
	<u>1</u>	<u>2</u>
0	0.390	0.390
3.8	0.290	0.275
7.5	0.210	0.195
11.3	0.159	0.140
15.0	0.110	0.100
18.8	0.085	0.072
22.5	0.060	0.050
$k_{obs} (sec^{-1})$	0.083	0.091
cc	1.000	0.999

$$[H_3O^+] = 1.43 \times 10^{-3}M$$

0	0.355	0.310
3.8	0.225	0.195
7.5	0.135	0.125
11.3	0.085	0.084
15.0	0.055	0.055
$k_{obs} (sec^{-1})$	0.116	0.115
cc	1.000	1.000

$$[H_3O^+] = 1.72 \times 10^{-3}M$$

0	0.330	0.117
3.8	0.195	0.103
7.5	0.117	0.060
11.3	0.075	0.033
15.0	0.040	-
$k_{obs} (sec^{-1})$	0.132	0.115
cc	0.999	0.965

$$[\text{H}_3\text{O}^+] = 2.00 \times 10^{-3}\text{M}$$

<u>Time(sec)</u>	<u>A-A_∞</u>	
	<u>1</u>	<u>2</u>
0	0.300	0.330
3.8	0.155	0.180
7.5	0.088	0.100
11.3	0.050	0.060
15.0	0.030	0.032
$k_{\text{obs}} (\text{sec}^{-1})$	0.153	0.153
cc	0.999	1.000

$$[\text{H}_3\text{O}^+] = 2.29 \times 10^{-3}\text{M}$$

0	0.210	0.280
3.8	0.109	0.135
7.5	0.058	0.065
11.3	0.030	0.032
15.0	0.015	0.015
$k_{\text{obs}} (\text{sec}^{-1})$	0.241	0.241
cc	1.000	1.000

B. $\mu = 0.05\text{M}$, $[(\text{CH}_3)_2\text{CoL}] = 10^{-4}\text{M}$

$$[\text{H}_3\text{O}^+] = 1.15 \times 10^{-3}\text{M}$$

0	0.335	0.379
3.8	0.225	0.245
7.5	0.140	0.155
11.3	0.090	0.110
15.0	0.060	0.072
18.8	0.040	0.050
k_{obs}	0.115	0.108
cc	1.000	0.999

B. $\mu = 0.05M$, $[(CH_3)_2CoL] = 10^{-4}M$

$$[H_3O^+] = 1.43 \times 10^{-3}M$$

<u>Time(sec)</u>	<u>1</u>	<u>A-A_∞</u> <u>2</u>
0	0.293	0.262
3.8	0.178	0.157
7.5	0.103	0.097
11.3	0.063	0.059
15.0	0.033	0.033
$k_{obs} (sec^{-1})$	0.137	0.132
cc	1.000	1.000

$$[H_3O^+] = 1.72 \times 10^{-3}M$$

0	0.320	0.245
3.8	0.151	0.120
7.5	0.075	0.062
11.3	0.040	0.031
15.0	0.020	-
$k_{obs} (sec^{-1})$	0.1850	0.1830
cc	0.999	1.000

$$[H_3O^+] = 2.00 \times 10^{-3}M$$

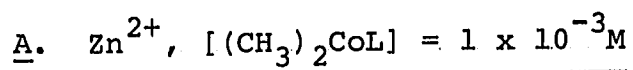
0	0.225	0.260
3.8	0.119	0.120
7.5	0.060	0.058
11.3	0.035	0.028
$k_{obs} (sec^{-1})$	0.168	0.235
cc	1.000	1.000

$$[\text{H}_3\text{O}^+] = 2.29 \times 10^{-3}\text{M}$$

<u>Time(sec)</u>	<u>A-A_∞</u>	
	<u>1</u>	<u>2</u>
0	0.250	0.213
3.8	0.100	0.077
7.5	0.041	0.035
11.3	0.015	0.013
k _{obs} (sec ⁻¹)	0.241	0.240
cc	1.000	1.000

APPENDIX IV

Kinetic data for methane evolution following the reactions of $(\text{CH}_3)_2\text{Co}(\text{BDML},3\text{pn})$ with excess Zn^{2+} , Cd^{2+} and Pb^{2+} .

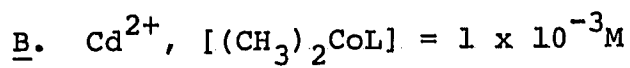


$$[\text{Zn}^{2+}] = 1 \times 10^{-3}\text{M}$$

<u>Time (hours)</u>	<u>$C_\infty - C$</u>	
	1	2
0.25	7.51	7.49
1.0	7.08	7.00
2.0	5.60	5.56
3.0	3.12	3.06
4.0	2.00	1.95
5.0	1.20	1.11
$k_{\text{obs}} (\text{sec}^{-1})$	1.12×10^{-4}	1.15×10^{-4}
cc	0.999	0.999

$$[\text{Zn}^{2+}] = 5 \times 10^{-3}\text{M}$$

0.25	7.28	7.20
1.0	5.96	5.84
2.0	3.60	3.51
3.0	2.32	2.22
4.0	1.52	1.45
5.0	0.88	0.76
$k_{\text{obs}} (\text{sec}^{-1})$	1.20×10^{-4}	1.31×10^{-4}
cc	0.999	1.000

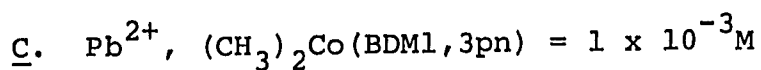


$$[\text{Cd}^{2+}] = 1 \times 10^{-3}\text{M}$$

<u>Time (hours)</u>	<u>$\frac{1}{C_\infty - C}$</u>	<u>$\frac{2}{C_\infty - C}$</u>
0	7.24	6.61
19.5	5.88	4.83
44.5	5.08	3.13
67.5	3.60	2.37
93.5	2.92	1.65
119.0	2.12	1.17
141.0	1.48	0.69
164.5	0.92	-
189.0	0.92	0.37
238.5	0.52	-
$k_{\text{obs}} (\text{sec}^{-1})$	3.82×10^{-6}	4.20×10^{-6}
cc	0.998	0.997

$$[\text{Cd}^{2+}] = 5 \times 10^{-3}\text{M}$$

<u>Time (hours)</u>	<u>$\frac{1}{C_\infty - C}$</u>
0	7.55
24	6.00
48	3.71
72	2.89
144	1.13
168	0.85
$k_{\text{obs}} (\text{sec}^{-1})$	3.72×10^{-6}
cc	0.998



$$[\text{Pb}^{2+}] = 1 \times 10^{-2}\text{M}$$

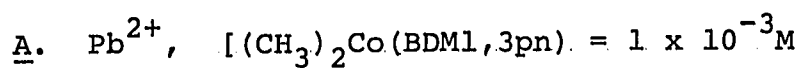
<u>Time (hours)</u>	<u>(C_∞-C)</u>	
	<u>1</u>	<u>2</u>
0	7.29	6.60
14.0	5.81	5.05
40.0	3.98	3.81
61.0	3.26	3.18
90.0	2.30	2.22
120.5	1.54	1.40
164.0	1.00	0.90
$k_{\text{obs}} (\text{sec}^{-1})$	3.25×10^{-6}	3.33×10^{-6}
cc	0.998	0.998

$$[\text{Pb}^{2+}] = 5 \times 10^{-3}\text{M}$$

<u>Time (hours)</u>	<u>(C_∞-C)</u>
0	7.29
14.0	6.15
40.0	4.40
61.0	3.60
90.0	2.61
120.5	1.75
164.0	1.19
$k_{\text{obs}} (\text{sec}^{-1})$	3.10×10^{-6}
cc	0.998

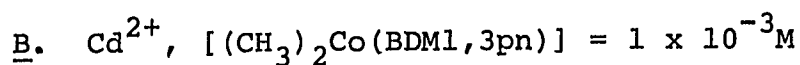
APPENDIX V

Kinetic data for methane evolution following the reactions of $(\text{CH}_3)_2\text{Co}(\text{BDMl},3\text{pn})$ with Cd^{2+} and Pb^{2+} in the molar ratio $([\text{M}^{2+}]/[\text{complex}])$ equal to 0.5.



$$[\text{Pb}^{2+}] = 5 \times 10^{-4}\text{M}$$

<u>Time (min.)</u>	<u>Disc</u>	
	<u>Integration</u>	
	1	2
2	0.10	0.14
4	0.31	0.25
6	0.41	0.38
8	0.49	0.50
10	0.59	0.60
15	1.00	0.94
20	1.23	1.18
30	1.71	1.64
40	1.98	1.92
85	2.51	2.64
780	3.28	3.32
2520	3.36	3.28
4320	3.41	3.36
8640	3.55	3.68
17280	3.54	3.66



$$[\text{Cd}^{2+}] = 5 \times 10^{-4}\text{M}$$

2	0.19	0.11
4	0.53	0.50
6	0.98	0.90
8	1.44	1.35
10	1.76	1.69
15	2.44	2.51
20	2.96	2.91
30	3.54	3.59
40	3.68	3.55
50	3.76	3.78
1410	5.04	5.11
2628	6.08	6.21
4152	7.04	7.15
5580	7.76	7.80
7170	8.00	7.99
8430	7.84	7.96
10710	7.68	7.81
12000	7.65	7.75